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Odorless, Regioselective Synthesis of Diaryl Sulfides and α-Thioaryl Carbonyls from Sodium Arylsulfinates *via* a Metal-Free Radical Strategy in Water

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Abstract: Regioselective arylthiolations of aromatic amines, arenols and ketones *via* C–H bond functionalization have been achieved with I_2 and PPh_3 in an aqueous system, whereby arylsulfenyl radicals are *in situ* generated from odorless sodium arylsulfinates. The arylsulfenyl radicals can react with free anilines containing electron-withdrawing groups and complex substrates (estrone and progesterone). Further experiments and quantum chemical calculations were also performed to deduce a mechanism for the formation of arylsulfenyl radicals.

Keywords: arylthiolation; diaryl sulfides; radical reaction; sodium arylsulfinates; α-thioaryl carbonyls

Introduction

Both diaryl sulfides[1] and α-thioaryl carbonyl compounds[2] are important and useful intermediates in organic synthesis as well as being ubiquitous in natural products, pharmacologically active compounds and organic materials. Traditionally, there are two main approaches for the preparation of diaryl sulfides. One is the transition metal-catalyzed cross-coupling of disulfides or thiols with aryl halides or pseudohalides.[3] Another method typically relies on the coupling of electrophilic sulfur reagents with organozinc or Grignard reagents.[4] In recent years, a series of regioselective methods for the direct C–H arylthiolation of arenes[5] or cyclohexanone[6] *via* electrophilic substitution routes to afford diaryl sulfides has been reported. Although the arylthiolations of various electron-rich arenes proceeded smoothly in these approaches, other arenes such as free anilines failed to yield the desired products.

Therefore, a metal-free protocol for the arylsulfuration of aromatic amines (especially free anilines) *via* direct aryl C–H bond functionalization appears desirable and synthetically attractive. Arylsulfenyl radicals seem to be an ideal species to achieve this goal since they are less electrophilic but more stable than the corresponding sulfenyl cations.[7] On the other hand, the classical methods for the formation of α-thioaryl carbonyl compounds include (i) the sulfanylation of enolates with various sulfanylating agents using strong bases;[8] (ii) the nucleophilic substitution of α-halogenated ketones with benzenethiols or disulfides;[9] and (iii) metal-catalyzed reactions for the construction of C–S bonds.[10] To eliminate the use of strong bases and metals, several metal-free strategies were developed for the synthesis of such compounds *via* nucleophilic α-sulfanylation of ketones, but thiols (or sulfur reagents pre-prepared from thiols) and organic solvents are the norm.[11] Based on these results, the quest for an efficient protocol using odorless sulfur reagents in green solvents is still ongoing.

With our interest in exploring new approaches for the construction of C–S bonds in water,[12] we disclose a metal-free radical route for the synthesis of diaryl sulfides and α-thioaryl carbonyl compounds using odorless and easy-to-handle sodium arylsulfinates as the sulfur source in an aqueous I_2/PPh_3 system. To the best of our knowledge,[13] this is the first example of the arylsulfanylation of free anilines and ketones using sodium arylsulfinates by a metal-free radical process in water. Further control experiments and quantum chemical calculations were also performed to gain insights into the generation mechanism of arylsulfenyl radicals in this system.

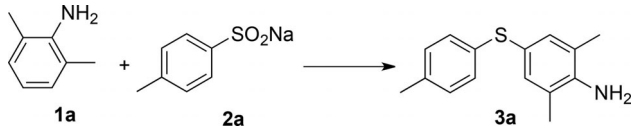
Results and Discussion

Initially, the coupling of 2,6-dimethylaniline **1a** with sodium *p*-tolylsulfinate **2a** was selected as the model reaction to optimize the reaction conditions (Table 1). After screening different solvents, water proved to be the best option (entry 8). Both I_2 and PPh_3 are necessary for the reaction. Diethyl phosphite in place of PPh_3 resulted in a lower yield of **3a** (entry 9). DMSO was also employed to reduce the amount of I_2,[14] but the results were unsatisfac tory (entry 10). Other sulfur sources including *p*-tolylthiol and 1,2-bis(4-tolyl)disulfane failed to yield the desired products in this system.

With the optimized conditions in hand, various amines and sodium arylsulfinates were chosen to establish the scope and generality of this protocol (Scheme 1). A series of electron-rich free anilines was subjected to the reaction conditions to produce the desired products (**3a**, **3b**, **3e**, **3f**, **3l**). To our delight, moderate to good yields were afforded in the cases of free anilines with electron-withdrawing groups (**3c**, **3d**, **3h**–**3k**), which failed to yield the desired products in the nucleophilic approaches. The reactions proceeded smoothly using *N*-substituted arylamines as the starting materials (**3m**–**3q**). Generally, the *para*-sulfanylarylamines were the main products, and traces of the disulfanyl products were obtained (**3b**, **3n**, **3p**) in some cases. For the *para*-substituted aromatic amines, *ortho*-sulfanyl products were obtained as the final products.

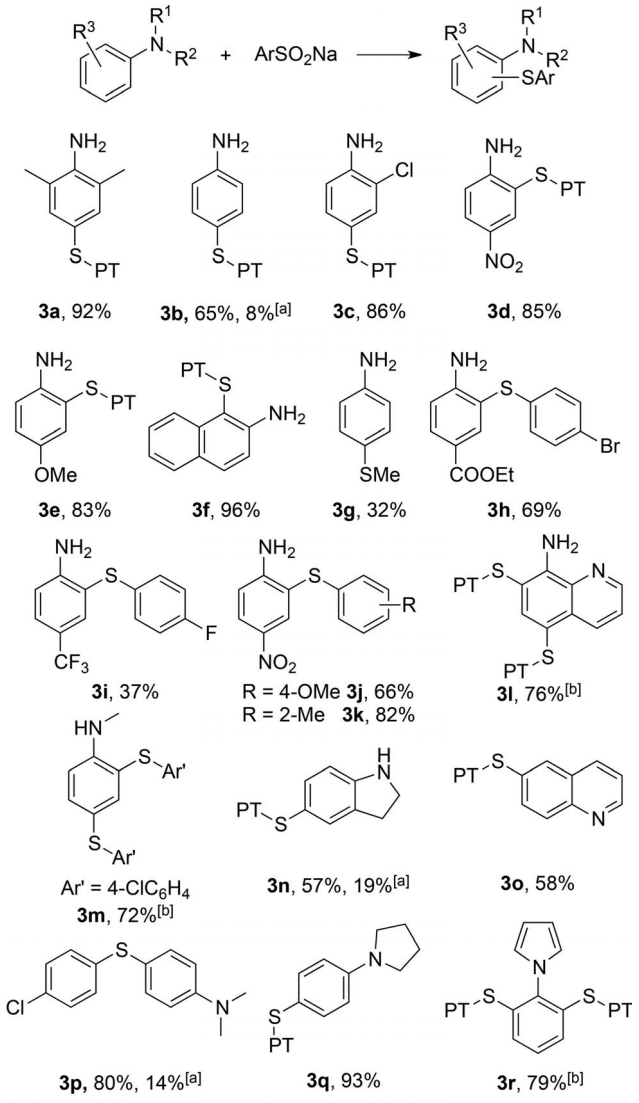
The reactions of quinolin-8-amine or *N*-methylaniline with sodium *p*-tolylsulfinate resulted in 2,4-disulfanylarylamines as the main products (**3l**, **3m**). Surprisingly, an aromatization product (**3o**) was derived when using 1,2,3,4-*tetra*-hydroquinoline as the substrate. A 2,6-disulfanyl product (**3r**) was afforded

Table 1. Optimization of the reaction conditions.[a]



Entry	Solvent	Yield [%][b]
1	toluene	45
2	THF	13
3	dioxane	30
4	DMSO	trace
5	DMF	54
6	EtOH	29
7	MeCN	trace
8	H_2O	92, 0,[c] 0[d]
9	H_2O	38[e]
10	H_2O	26[f]
11	H_2O	trace[g]
12	H_2O	trace[h]

[a] *Conditions:* **1a** (0.25 mmol), **2a** (0.30 mmol), I_2 (0.25 mmol), PPh_3 (0.60 mmol), H_2O (1.0 mL), 100 °C, 12 h.
[b] Isolated yields.
[c] Without I_2.
[d] Without PPh_3.
[e] Diethyl phosphite in place of PPh_3.
[f] DMSO (3 equiv.) and I_2 (20 mol%) in place of I_2 (1 equiv.).
[g] *p*-Tolylthiol in place of sodium *p*-tolylsulfinate was used.
[h] 1,2-Bis(4-tolyl)disulfane in place of sodium *p*-tolylsulfinate was used.



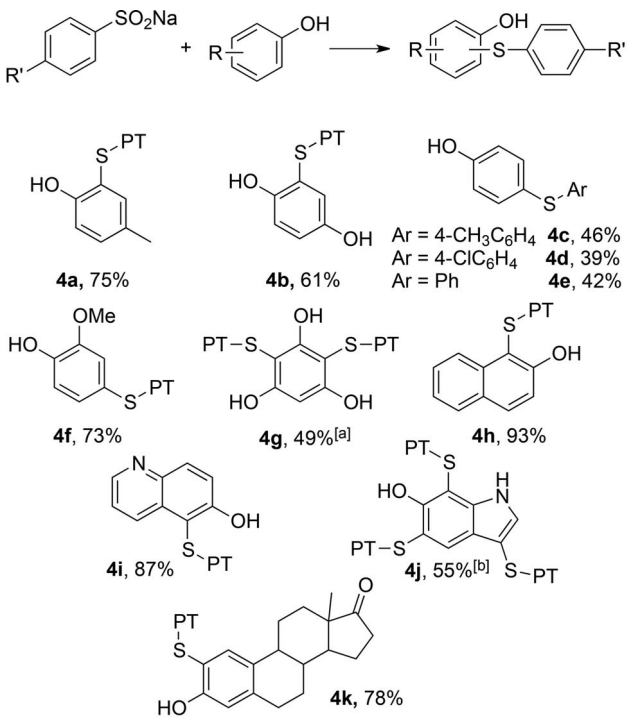
[a] The yields of 2,4-disulfanylarylamines.
[b] *Conditions:* amine 0.25 mmol, sodium arylsulfinate 0.6 mmol, I_2 0.5 mmol, PPh_3 1.2 mmol, H_2O 2.0 mL, 100 °C, 12 h.

Scheme 1. The reaction of arylamines with sodium arylsulfinates in water. PT = *p*-tolyl. *Conditions:* amine (0.25 mmol), sodium arylsulfinate (0.30 mmol), I_2 (0.25 mmol), PPh_3 (0.6 mmol), H_2O (1.0 mL), 100 °C, 12 h. Isolated yields are reported.

when 1-phenyl-1*H*-pyrrole was used as the substrate. Sodium methanesulfinate was also applied in the reaction to gain a poor yield of the desired product (**3g**).

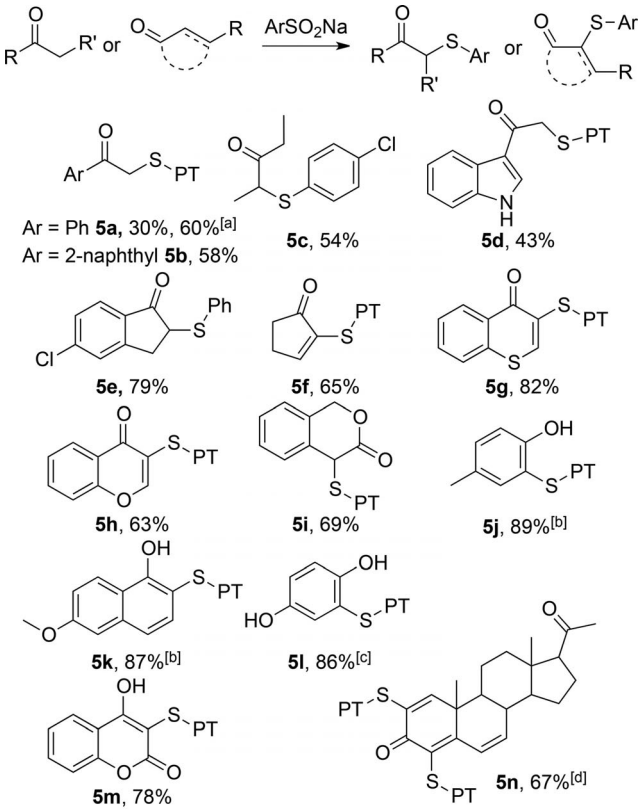
In the view of the similar reactivity of arenols with aromatic amines, we next sought to study the sulfanylation of arenols (Scheme 2). Generally, the electron-rich phenols should undergo the sulfanylation to furnish the products (**4a**–**4i**) in moderate to good yields. However, no reaction took place in the cases of the phenols with electron-withdrawing groups (such as nitro and trifluoromethyl groups). An excellent *para*-selectivity of the sulfanylation was observed (**4c**–**4f**), meanwhile only *ortho*-substituted products were provided when arenols bearing *para* groups were used (**4a**, **4b**, **4h**, **4i**, **4k**). In the cases of benzene-1,3,5-triol and 1*H*-indol-5-ol, disulfanyl (**4g**) and trisulfanyl products (**4j**) were yielded, respectively. A complex phenol (estrone) was also applied in the protocol to afford the desired product (**4k**).

With the successful development of the sulfanylation of arenes, further investigations were made to realize the sulfanylation of ketones with sodium arylsulfinates *via* C–H functionalization (Scheme 3). Linear ketones could react with sodium arylsulfinates to form α-arylthio ketones (**5a**–**5d**) in low to moderate yields. Cyclic ketones exhibit better reactivity than linear ones (**5e**–**5h**, **5j**–**5l**). It should be noted that unexpected α-sulfanyl enones (**5f**–**5h**) and 2-sulfanylarenols (**5j**–**5l**) were generated under the optimized conditions, presumably owing to the iodine-induced oxydehydrogenations.[6] The scope was also extended to other cyclic carbonyl compounds, such as isochroman-3-one and 4-hydroxycoumarin (**5i**, **5m**). Encouraged by the broad generality of this protocol, we sought to demonstrate its applicability in more complex ketones. To our delight, a disulfanyl product (**5n**) was obtained when progesterone was subjected to the identical conditions. Interestingly, a sulfanylfuran (**5o**) was obtained from cyclopropyl(phenyl)methanone with sodium *p*-tolylsulfinates through a ring-opening and recyclization route (Scheme 4).



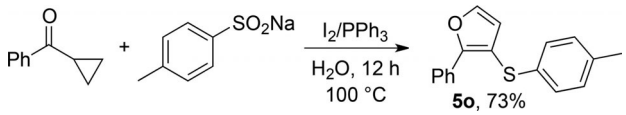
[a] *Conditions:* sodium *p*-tolylsulfinate 0.60 mmol, benzene-1,3,5-triol 0.25 mmol, I_2 0.50 mmol, PPh_3 1.2 mmol, H_2O 2.0 mL, 100 °C, 12 h.
[b] *Conditions:* sodium *p*-tolylsulfinate 0.90 mmol, 1*H*-indol-6-ol 0.25 mmol, I_2 0.75 mmol, PPh_3 1.8 mmol, H_2O 3.0 mL, 100 °C, 12 h.

Scheme 2. The sulfanylation of arenols with sodium arylsulfinates. PT = *p*-tolyl. *Conditions:* sodium arylsulfinate (0.30 mmol), arenol (0.25 mmol), I_2 (0.25 mmol), PPh_3 (0.60 mmol), H_2O (1.0 mL), 100 °C, 12 h. Isolated yields are reported.



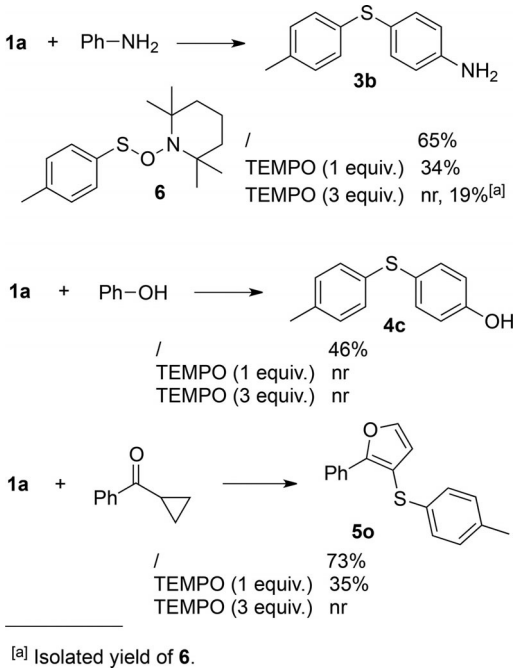
[a] At 130 °C.
[b] The corresponding cyclohexanone as the substrate.
[c] Benzoquinone as the substrate.
[d] *Conditions:* sodium *p*-tolylsulfinate 0.60 mmol, progesterone 0.25 mmol, I_2 0.50 mmol, PPh_3 1.2 mmol, H_2O 2.0 mL, 100 °C, 12 h.

Scheme 3. The reactions of sodium arylsulfinates with ketones. PT = *p*-tolyl. *Conditions:* sodium arylsulfinate (0.30 mmol), ketone (0.25 mmol), I_2 (0.25 mmol), PPh_3 (0.60 mmol), H_2O (1.0 mL), 100 °C, 12 h. Isolated yields are reported.



Scheme 4. The reaction of cyclopropyl(phenyl)methanone with sodium *p*-tolylsulfinates in water.

To probe the mechanism, radical trapping experiments were designed and investigated (Figure 1). All the reactions were inhibited in the presence of the radical trap TEMPO. Radical trapping product **6** was observed by GC-MS, separated and further identified



[a] Isolated yield of **6**.

Figure 1. The radical trapping experiments. *Conditions:* **1a** (0.30 mmol), aniline, phenol or cyclopropyl(phenyl)methanone (0.25 mmol), I_2 (0.25 mmol), PPh_3 (0.60 mmol), H_2O (1 mL), 100 °C, 12 h. Isolated yields are reported.

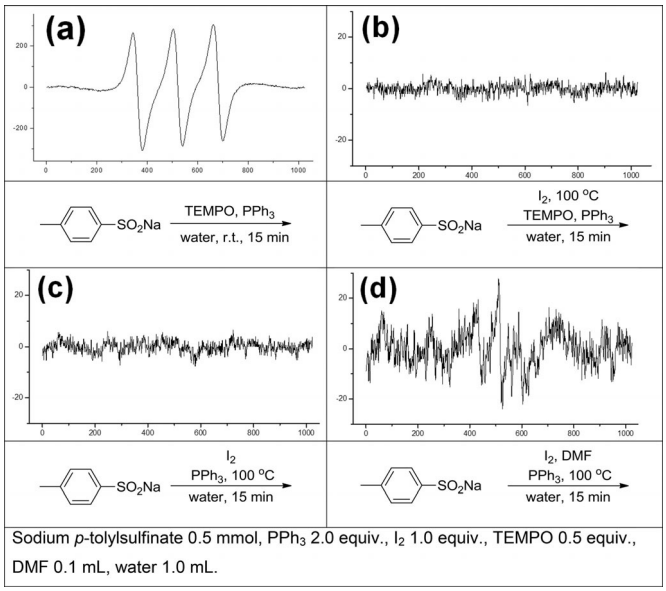
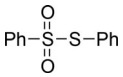
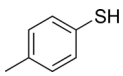


Figure 2. EPR results in the system of I_2/PPh_3.

by ^1H and ^{13}C NMR spectra suggesting that these transformations may involve radical processes. To further certify the radical process in the system, electron paramagnetic resonance (EPR) experiments were also performed. The TEMPO signals disappeared when both I_2 and PPh_3 were employed in aqueous systems (Figure 2, a *vs.* b). Weak radical signals were detected in the system of I_2/PPh_3 when DMF was added (c *vs.* d), so DMF may play a role as the radical stabilizer in this system.

Based on these results, it can be concluded that free radicals are generated in the system of I_2/PPh_3. Further control experiments were carried out to confirm whether *S*-phenyl benzene sulfonothioate, 1,2-di-*p*-tolyl disulfane or 4-methylbenzenethiol were the intermediates in this system (Table 2). It was found that no or poor yields of the final products were afforded in most cases. Although the desired products could be

Table 2. Control experiments for the probable reaction intermediates.[a]

Entry	Intermediate	Substrate	Yield [%][b]	Yield [%][b,c]
1		acetophenone	nr	–
2		phenol	10	trace
3		aniline	61	63
4		acetophenone	nr	–
5	1,2-bis(4-chlorophenyl)disulfane	phenol	nr	–
6		aniline	nr	–
7		acetophenone	nr	–
8		phenol	nr	–
9		aniline	nr	–

[a] The reaction conditions were the optimized conditions except that sodium *p*-tolylsulfinate was used instead of the intermediates.
[b] The yields were determined by GC-MS.
[c] 3 equiv. TEMPO were used in these reactions.

Table 3. The calculated values of the BDEs of some possible intermediates based on quantum calculations.

Compound	Dissociation bond	BDE [kJ/mol]
Ph–S–I	S–I	190.35
I_2	I–I	171.02 (151)[a]
PhS–SPh	S–S	228.14
Br_2	Br–Br	190.09 (192)[a]

[a] Actual measured value.

obtained with moderate yields in the reaction of aniline with *S*-phenyl benzenesulfonothioate, the reaction did not involve a radical route. Thus, all of them proved to be not the intermediates in the system.

According to the calculation results of the bond dissociation energies (BDEs) (Table 3), it can be concluded that both homolyses of I_2 and PhSI are likely to occur to form phenylthio radicals in the I_2/PPh_3 system.[12a,15] On the basis of the results above and previous literature reports, a mechanism was proposed for the formation of arylsulfenyl radicals in the I_2/PPh_3 system and is illustrated in Figure 3. At first, reduction of sodium arylsulfinate mediated by a combination of I_2 and PPh_3 results in ArSI.[16] Then, arylsulfenyl radicals are formed *via* the homolysises of I_2 or ArSI in the I_2/PPh_3 system. Meanwhile, polar processes may also exist in these transformations as the minor pathways.

Although the detailed mechanisms of these reactions remain to be elucidated, a tentative pathway for C–H arylthiolation of arenes is proposed (Figure 4). Firstly, an arylsulfenyl radical adds to the arene to produce radical intermidate **7** (*o*-substituted) or **8** (*p*-substituted). Then, the *o*-substituted product (or *p*-substituted product) is formed by the reaction of ArSI and **7** (or **8**) following the formation of an arylsulfenyl radical and HI.[5,12a]

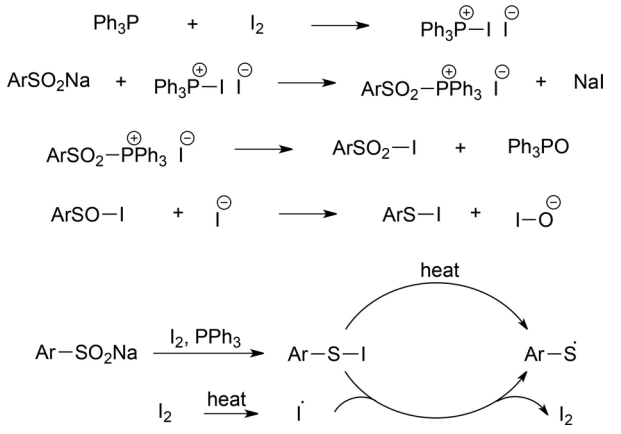


Figure 3. The proposed mechanism of formation of arylsulfenyl radicals from sodium arylsulfinates in the I_2/PPh_3 system.

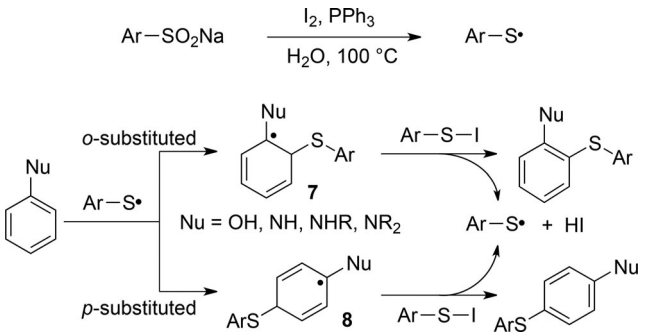


Figure 4. A tentative pathway for the arylthiolation of arenes with sodium arylsulfinates in the I_2/PPh_3 system.

Conclusions

In summary, we have introduced an efficient aqueous system for the regioselective synthesis of diaryl sulfides and α-thioaryl carbonyls from sodium arylsulfinates, in which no metal, organic solvent or evil smelling thiol is required. Electron-deficient free anilines and complex subtrates (estrone and progesterone) can be applied in the protocol owing to the high reactivity of the *in situ* generated arylsulfenyl radicals. The experiments and quantum calculations were also performed to gain insights into the generation mechanism of arylsulfenyl radicals. Moreover, this sulfuration chemistry has the potential to promote the discovery of other new radical sulfuration reactions for the construction of organosulfur compounds.

Experimental Section

General Procedure for the Synthesis of 3 and 4

A mixture of sodium arylsulfinate (0.30 mmol), phenol or aromatic amine (0.25 mmol), I_2 (0.25 mmol) and PPh_3 (0.60 mmol) in water (1.0 mL) was stirred at 100 °C for 12 h. Upon completion, the reaction mixture was diluted with EtOAc (4.0 mL), filtered through a bed of silica gel layered over Celite. The volatiles were removed under vacuum to afford the crude product. Further column chromatography on silica gel (EtOAc/petroleum ether) was needed to afford the pure desired product **3** or **4**.

General Procedure for the Synthesis of 5

A mixture of sodium arylsulfinate (0.30 mmol), ketone (0.25 mmol), I_2 (0.25 mmol) and PPh_3 (0.60 mmol) in water (1.0 mL) was stirred at 100 °C for 12 h. Upon completion, the reaction mixture was diluted with EtOAc (4.0 mL), filtered through a bed of silica gel layered over Celite. The volatiles were removed under vacuum to afford the crude product. Further column chromatography on silica gel (EtOAc/petroleum ether) was needed to afford the pure desired product **5**.

Acknowledgements

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[5] All the reactions in the article are C–H arylthiolations of arenes, which should be C–H functionalizations, although no direct H-abstraction process exists during these reactions. For selected monographs on the direct C–H arylthiolation of arenes by electrophilic substitution routes, see: a) T. Hostier, V. Ferey, G. Ricci, D. Gomez Pardo, J. Cossy, *Org. Lett.* **2015**, *17*, 3898–3901; b) S. K. R. Parumala, R. K. Peddinti, *Green Chem.* **2015**, *17*, 4068–4072; c) F. Xiao, S. Chen, J. Tian, H. Huang, Y. Liu, G.-J. Deng, *Green Chem.* **2016**, *18*, 1538–1546; d) X. Zhao, T. Li, L. Zhang, K. Lu, *Org. Biomol. Chem.* **2016**, *14*, 1131–1137; e) S. Saba, J. Rafique, A. L. Braga, *Catal. Sci. Technol.* **2016**, *6*, 3087–3098; f) Q. Wu, D. Zhao, X. Qin, J. Lan, J. You, *Chem. Commun.* **2011**, *47*, 9188–9190; g) D. Wang, R. Zhang, S. Lin, Z. Yan, S. Guo, *RSC Adv.* **2015**, *5*, 108030–108033.

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