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Synthesis of Thioethers and Thioesters with Alkyl Arylsulfinates as the Sulfenylation Agent under Metal-free Conditions

Yahui Li,[a] Fengxiang Zhu,[a] Zechao Wang,[a] and Xiao-Feng Wu*[a]

Abstract: An interesting study on the coupling of cycloalkanes with alkyl arylsulfinates has been performed. With iodine as the catalyst, through $C_{(sp3)}$-H bond activation and sulfinates reduction, a wide range of thioethers were produced in moderate to high yields. Additionally, various thiocarboxylic esters can be produced as well by just perform the reaction under CO pressure. Notably, this is the first report on using alkyl arylsulfinates as the sulfenylation agent in cross-coupling transformation.

Sulfur-containing compounds are of great importance as building blocks for natural products, pharmaceuticals and functional materials (Figure 1).[1] Consequently, the development of new synthetic methodology for organosulfur compounds synthesis is an important field in organic chemistry.[2] Indeed, numerous novel procedures have been established during the past decades. In general, the developed procedures can be divided into two classes; either based on sulfur sources (A + 'S' + B = A'S'B)[3] or with sulfenylation agents (A'S'X + B = A'S'B). Concerning the sulfenylation agents, disulfides,[4] sulfenyl halides,[5] *N*-thioarylphthalimides,[6] thiols,[7] arylsulfonyl cyanides,[8] quinone mono-*O*,*S*-acetals,[9] sulfonyl hydrazides,[10] arylsulfonyl chlorides,[11] sodium sulfinates[12] and sulfinic acid[13] have been reported and applied in various transformations. Alkyl arylsulfinates is an interesting class of organic compounds which is ready available, odour-less, stable and miscible with organic solvents.[14] However, the usage of alkyl arylsulfinates as sulfenylation agent has been rarely explored.

On the other hand, carbonylative transformations have already become a powerful toolbox in modern organic synthesis.[15] Through carbonylation reactions, CO as one of the cheapest C1 source can be easily installed into the parent molecules. By this manner, the carbon chain can be easily prolonged while the produced carbonyl-containing compounds are important chemicals as well. In all the developed carbonylation reaction, regarding the coupling partners applied, nitrogen, oxygen and carbon nucleophiles are more frequently applied. The using of 'S' as nucleophile in carbonylation reactions are less explored which might due to the non-pleasant smell of thiols and also its poison to the metal catalysts.[16] Taking all these backgrounds into consideration and also as our continual interests on carbonylation chemistry, we performed this study on using alkyl arylsulfinates as the sulfenylation agent. With cycloalkanes as the reaction partners, the corresponding carbonylated and non-carbonylated products were formed in moderate to good yields. This study hold the following features: 1) with iodine as the catalyst in carbonylative coupling; 2) metal-free activation of $C_{(sp3)}$-H bond of simple cycloalkanes; 3) the first example on using methyl arylsulfinates as the sulfenylation agent.

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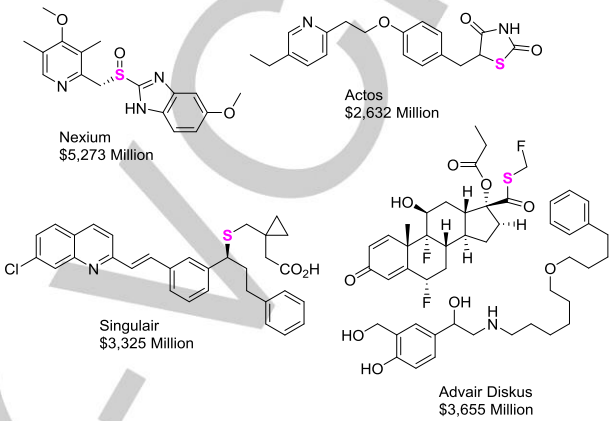
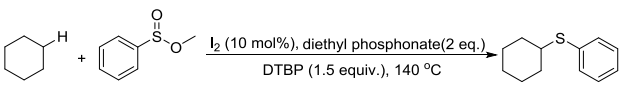


Figure 1. Selected examples of organosulfur-containing drugs.

Our investigation started with methyl benzenesulfinate and cyclohexane as the model substrates under at 140 °C with iodide as the catalyst (Table 1). By optimizing the possible reaction parameters, the combination of I_2 (10 mol%), diethyl phosphonate (2 equiv.) and DTBP (1.5 equiv.) were found to be the best catalyst system here. Under this conditions, 82% of cyclohexyl(phenyl)sulfane can be successfully isolated (Table 1, entry 1). The results of control experiments in the absence of iodine, diethyl phosphonate or DTBP indicated that these species play indispensable roles in the reaction (Table 1, entries 2-7). Other oxidant such as TBHP, H_2O_2, cumyl hydroperoxide, benzoyl peroxide, *tert*-butyl peroxybenzoate provided less reaction efficiency (Table 1, entries 8-12). Remove of MeCN or decrease reaction temperature all gave decreased yields (Table 1, entries 13-15). Additionally, in order to exclude the metal impurities in the reagents act as the real catalyst, inductively coupled plasma atomic emission spectroscopy (ICP–AES) analysis of the reaction reagents were performed. The results shown the concentrations of the possible transition metals, such as Cu, Pd, Rh, Ru, and Ni were below the detection limitation (see the Supporting Information for details). These results confirmed the catalyst role of iodine in this procedure, and excluded the effects of the possible transition metal contaminations in reagents applied.

Table 1. Iodine-catalyzed cyclohexane activation: Optimization reaction conditions.[a]



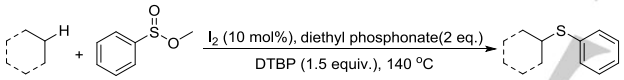
Entry	Variation from standard conditions (3a)	Yield
1	Standard Condition	82%
2	5 mol% of I_2	70%
3	20 mol% of I_2	80%
4	Without I_2	18%

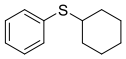
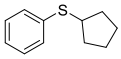
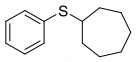
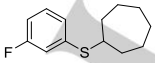
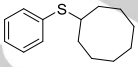
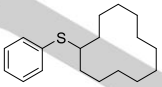
5	Without DTBP	0%
6	Diethyl phosphonate (1 eq.)	48%
7	Without diethyl phosphonate	32%
8	TBHP instead of DTBP	20%
9	H_2O_2 instead of DTBP	trace
10	Benzoyl peroxide instead of DTBP	trace
11	Cumyl hydroperoxide instead of DTBP	trace
12	*tert*-Butyl peroxybenzoate instead of DTBP	10%
13	Without CH_3CN	56%
14	120 ^oC	48%
15	100 ^oC	trace

[a] Methyl benzenesulfinate (0.5 mmol), I_2 (10 mol%), diethyl phosphonate (2 equiv.), DTBP (0.75 mmol; 1.5 equiv.), cyclohexane/CH_3CN (1.5 mL/0.2 mL), 140 ^oC, 24 h, isolated yields.

With the optimized reaction conditions in hand, we examined the scope of the reaction. Cycloalkanes were tested at the first stage (Table 2) and moderate to good yields can be achieved in general. Not only cyclopentane, but larger sized rings are all suitable substrates here. However, cyclic ethers (1,4-dioxane, THF) and cyclic amines (piperidine, 1-methylpiperidine, pyrrolidine) failed under our conditions.

Table 2. Iodine-catalyzed thioethers synthesis from alkanes.

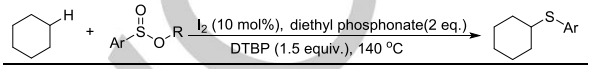


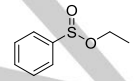
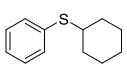
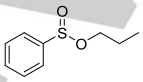
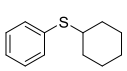
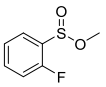
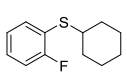
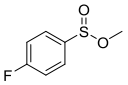
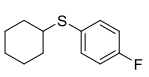
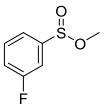
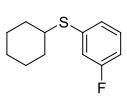
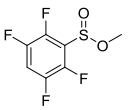
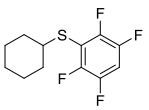
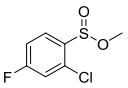
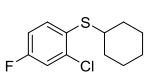
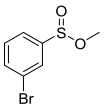
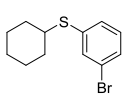
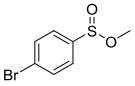
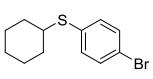
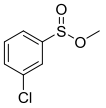
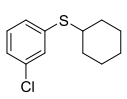
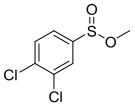
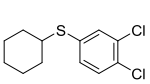
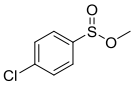
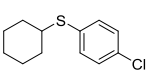
Entry	Alkanes	Products	Yield
1			82%
2			56%
3			61%
4			75%
5			51%
6			73%

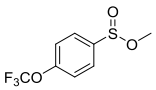
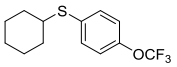
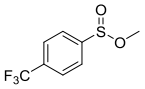
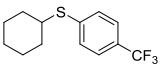
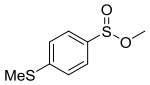
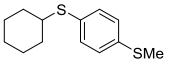
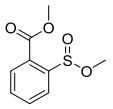
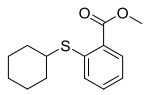
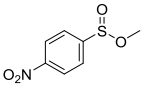
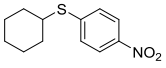
[a] Methyl benzenesulfinate (0.5 mmol), I_2 (10 mol%), diethyl phosphonate (1 mmol), DTBP (0.75 mmol), alkane/CH_3CN (1.5 mL/0.2 mL), 140 ^oC, 24 h, isolated yields.

Regarding the applicable alkyl benzenesulfinates, except methyl benzenesulfinate, ethyl benzenesulfinate and propyl benzenesulfinate are applied and give the corresponding products in good yields successfully (Table 3, entries 1-2). Then various methyl arylsulfinates were tested under the optimized reaction conditions. Fluoro substituted methyl arylsulfinates gave the desired thioethers in good yields (Table 3, entries 3-7). Good to excellent yields of bromo and chloro substituted products can be produced as well; these products are ready for further functionalization via cross-coupling reactions (Table 3, entries 8-12). Good yields of cyclohexyl(4-(trifluoromethoxy)phenyl)sulfane and cyclohexyl(4-(trifluoromethyl)phenyl)sulfane were isolated without any further optimizations (Table 3, entries 13 and 14). 76% yield of cyclohexyl(4-(methylthio)phenyl)sulfane can be produced under identical reaction conditions (Table 3, entry 15). Ester functional group can also be tolerated and gave the corresponding product in 72% yield (Table 3, entry 16). However, decreased yield was obtained with nitro substituted substrate (Table 3, entry 17).

Table 3. Iodine-catalyzed thioethers synthesis from arylsulfinates.[a]



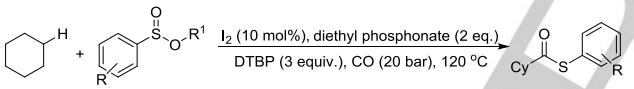
Entry	Arylsulfinates	Products	Yield
1			75%
2			72%
3			86%
4			74%
5			71%
6			61%
7			87%
8			89%
9			66%
10			88%
11			93%
12			75%

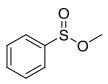
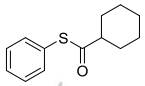
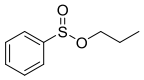
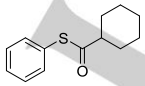
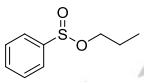
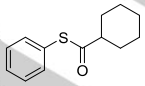
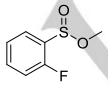
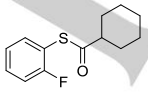
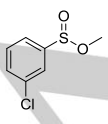
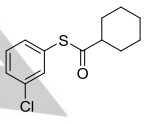
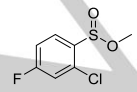
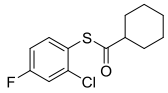
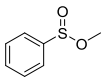
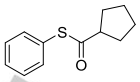
13			65%
14			79%
15			76%
16			72%
17			32%

[a] Arylsulfinates (0.5 mmol), I_2 (10 mol%), diethyl phosphonate (1 mmol), DTBP (0.75 mmol), cyclohexane (1.5 mL), MeCN (0.2 mL), 140 ^{o}C, 24 h, isolated yields.

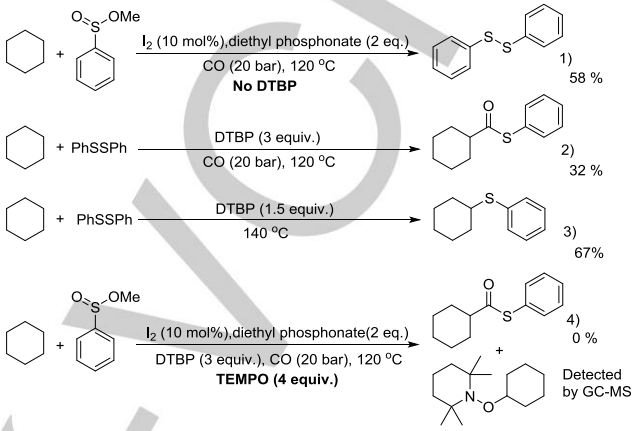
As our interests in carbonylation chemistry, we performed the same reaction under CO pressure. To our delight, the desired thioester can be successfully produced (Table 4). By increasing the loading of DTBP and decreasing the reaction temperature, 59% of the desired product can be formed (Table 4, entry 1). For the success of this transformation, 20 bar of CO pressure is necessary. Lower pressure gave lower yield of thioester and thioether can also be detected. Moderate yields of thioesters can be obtained in general in substrates testing.

Table 4. Iodine-catalyzed thioesters synthesis.[a]



Entry	Arylsulfinates	Products	Yield
1			59%
2			57%
3			54%
4			44%
5			40%
6			50%
7			53%

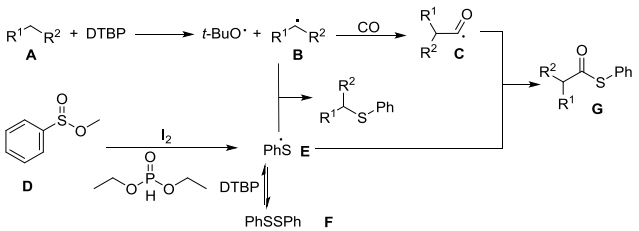
[a] Arylsulfinates (0.5 mmol), I_2 (10 mol%), diethyl phosphonate (1 mmol), DTBP (1.5 mmol), CO (20 bar), cyclohexane/CH_3CN (1.5 mL/0.2 mL), 120 ^{o}C, 24 h, isolated yields.



Scheme 1. Control experiments.

In order to get insight into the reaction mechanism, some control experiments were carried out and shown in Scheme 1. When no DTBP was added into the reaction, no desired thioether or thioester can be obtained but 58 % yield of phenyl disulfide was isolated (Scheme 1, eq. 1). Also cyclohexane can react with phenyl disulfide (Scheme 1, eq. 2 and eq. 3). When 4 equivalents of TEMPO were added to the standard reaction mixture, no desired product can be obtained (Scheme 1, eq. 4). And a product from the reaction between cyclohexane and TEMPO can be found in GC-MS analysis. These results indicate that the reaction proceeds through radical intermediates and phenyl disulfide can be the resting state of the sulfinates reduction process.

Based on these results, a possible reaction mechanism is proposed (Scheme 2). The reaction started with a thermal homolytic cleavage of a peroxide to generate the *tert*-butoxy radical, which reacts with cyclohexane **A**. After CO insertion into the radical **B**, intermediate **C** can be formed. Meanwhile, methyl benzenesulfinate **D** is reduced by diethyl phosphonate and I_2 to generate the phenyl thiol radical **E**, which is considered as the resting state of phenyl disulfide. Finally, **C** reacts with **E** to afford the final product **G**.



Scheme 2. Proposed reaction mechanism.

In conclusion, an interesting study on the coupling of cycloalkanes with alkyl arylsulfinates has been performed. With iodine as the catalyst, through $C_{(sp3)}$-H bond activation and sulfinates reduction, a wide range of thioethers were produced in moderate to high yields. Additionally, various thiocarboxylic

esters can be produced as well by just perform the reaction under CO pressure. Notably, this is the first report on using alkyl arylsulfinates as the sulfenylation agent in cross-coupling transformation.

Experimental Section

General procedure A: A 25-mL pressure tube was charged with 0.5 mmol of methyl benzenesulfinate, 10 mol% of I_2, 1 mmol of diethyl phosphonate, 0.75 mol of DTBP and cyclohexane/CH_3CN (1.5 mL/0.2 mL). Then the tube was sealed and the mixture was heated under stirring at 140 ^oC for 24 h. After this time the mixture was cooled to room temperature and the mixture was concentrated under vacuum. The pure products were obtained after purification by column chromatography (pentane).

General procedure B: A 4 mL screw-cap vial was charged with 0.5 mmol of methyl benzenesulfinate, 10 mol% of I_2, 1 mmol of diethyl phosphonate and an oven-dried stirring bar. The vial was closed by Teflon septum and phenolic cap and connected with atmosphere with a needle. After cyclohexane/CH_3CN (1.5 mL/0.2 mL), DTBP (0.75 mmol) were injected by syringe, the vial was fixed in an alloy plate and put into Paar 4560 series autoclave (300 mL) under argon atmosphere. At room temperature, the autoclave is flushed with carbon monoxide for three times and 20 bar of carbon monoxide was charged. The autoclave was placed on a heating plate equipped with magnetic stirring and an aluminum block. The reaction is allowed to be heated under 120 ^oC for 24 hours. Afterwards, the autoclave is cooled to room temperature and the pressure was carefully released. After removal of solvent under reduced pressure, pure product was obtained by column chromatography on silica gel (eluent: pentane/ethyl acetate = 250:1).

Acknowledgements

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Keywords: arylsulfinates • sulfenylation agent • green chemistry • domino reaction • carbonylation

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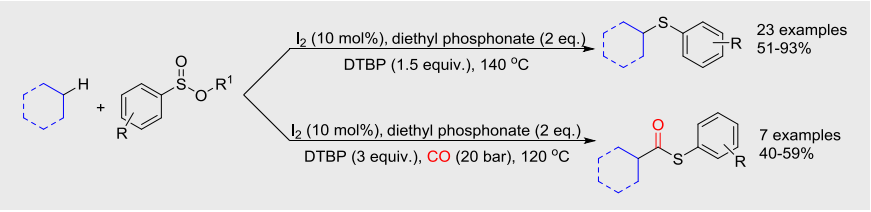

An interesting study on the coupling of cycloalkanes with alkyl arylsulfinates has been performed. With iodine as the catalyst, through $C_{(sp3)}$-H bond activation and sulfinates reduction, a wide range of thioethers were produced in moderate to high yields. Additionally, various thiocarboxylic esters can be produced as well by just perform the reaction under CO pressure. Notably, this is the first report on using alkyl arylsulfinates as the sulfenylation agent in cross-coupling transformation.

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Synthesis of Thioethers and Thioesters with Alkyl Arylsulfinates as the Sulfenylation Agent under Metal-free Conditions