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Odorless, One-Pot Regio- and Stereoselective Iodothiolation of Alkynes with Sodium Arenesulfinates under Metal-Free Conditions in Water

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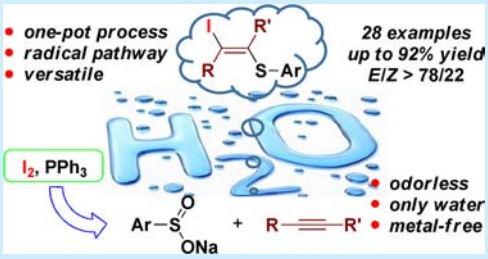
Supporting Information

ABSTRACT: A newly developed regio- and stereoselective radical addition of alkyne under metal-free conidtions has been disclosed. This chemistry, in which odorless sodium arenesulfinates in place of thiols are used as the sulfur reagent, provides an efficient, one-pot approach for the generation of β-iodoalkenyl sulfides, which can be easily further functionalized to derive various alkenes and alkynyl sulfides rendering this methodology attractive to both synthetic and medicinal chemistry.



Vinyl sulfides have found a widespread utilization as convenient intermediates in organic chemistry[1] and materials chemistry,[2] meanwhile many natural products and compounds exhibiting remarkable biological properties contain the vinyl sulfide moiety.[3] Thus, numerous synthetic methods have been reported for the preparation of these compounds.[4] Owing to the well-known nucleophilic substitution and cross-coupling importance and utility of halides (especially iodides), it is significant and interesting on incorporation of halides and the vinyl sulfides into organic compounds by one-pot means. Although β-haloalkenyl sulfides are useful intermediates to prepare various alkenes by the transformation of halogeno moieties and the C−S bond cleavage,[5] the advances of their synthetic methods have not been well-performed to date.

Typically, β-haloalkenyl sulfides are synthesized by the addition of sulfenyl halides to alkynes.[6] For example, Nishihara's group has reported that the chlorothiolation of terminal alkynes could afford *syn* adducts catalyzed by palladium[6a] and result in *anti* adducts via a radical process induced by iron.[6b] Nevertheless, several issues of these strategies should be addressed: (1) most of the sulfenyl halides (especially sulfenyl iodides) are really unstable compounds; (2) the formation of sulfenyl halides requires toxic and hard to handle chlorine (or bromine) or smell thiols; (3) the synthesis of β-iodoalkenyl chalcogenides has not been well-studied.

In order to eliminate these problems, a copper-catalyzed synthesis of β-haloalkenyl chalcogenides by the addition of disulfides to internal alkynes have been reported by Taniguchi.[7] The approach proves to be an efficient route to generate β-haloalkenyl sulfides using disulfides in place of sulfenyl halides, but in the view of green chemistry, it also encounters disadvantages, such as prepreparation of disulfides from thiols, the use of transition metal catalysts and toxic organic solvents, and limited substrate scope of terminal alkynes and iodothiolation adducts. With our interests in exploring odorless protocols for the formation of C−S bonds[8] and designing organic reactions in water,[9] we envisage to explore an odorless and metal-free route for regio- and stereoselective formation of β-iodoalkenyl sulfides in water.

On the one hand, several attempts have been made for the construction of C−S bonds using sodium arenesulfinates,[10] aryl sulfochlorides,[11] and aryl sulfonyl hydrazide[12] as the sulfur sources under reduction conditions. On the other hand, sodium arenesulfinates can react with aryl acetylenes to afford different sulfones under diverse conditions (Figure 1, *path A*). Generally,

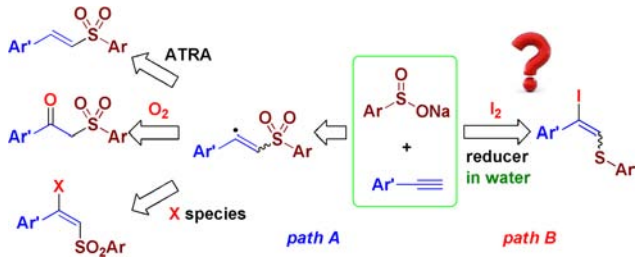


Figure 1. Transformations of sodium arenesulfinates with aryl acetylenes under diverse conditions.

vinyl sulfones are obtained from a reactive vinyl radical by atom transfer radical addition (ATRA).[13] The reactive vinyl radical can be trapped by dioxygen due to its diradical structure to yield β-keto sulfones.[14] β-haloalkenyl sulfones are generated through similar processes in the presence of halide species.[15] Based on these results, we reason that sodium arenesulfinates can be easily reduced to reactive aryl sulfide species, which

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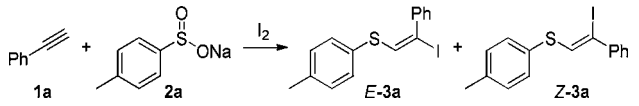
might add to aryl acetylene with iodine to derive β-iodoalkenyl sulfides (*path B*).

To verify the feasibility of our proposed assumption, we started the investigation by selecting the reaction of phenylacetylene **1a** with sodium *p*-toluenesulfinate **2a** as the model reaction (Table 1). Not surprisingly, the reaction provided a

Table 1. Optimization of Reaction Conditions[a]



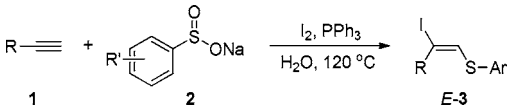
entry	reducer	solvent	yield (%)[b,c]	E/Z[c]
1	$OPH(OC_2H_5)_2$	toluene	trace	/
2	PPh_3	toluene	20	85/15
3	HCOOH	toluene	trace	/
4	$N_2H_4{\cdot}H_2O$	toluene	0	/
5	Zn	toluene	0	/
6	PPh_3	1,4-dioxane	18	86/14
7	PPh_3	EtOH	40	89/11
8	PPh_3	anisole	59	92/8
9	PPh_3	*t*-BuOH	24	88/12
10	PPh_3	ether	trace	/
11	PPh_3	MeOH	64	86/14
12	PPh_3	glyme	49	83/17
13	PPh_3	MeCN	trace	/
14	PPh_3	DMF	65	87/13
15	PPh_3	THF	trace	/
16	**PPh_3**	**H_2O**	**87**	**93/7**
17	PPh_3	H_2O	10[d]	/
18	PPh_3	H_2O	0[e]	/

[a]Reaction conditions: phenylacetylene 0.250 mmol, sodium *p*-toluenesulfinate 0.375 mmol, I_2 0.375 mmol, reductant 3 equiv, solvent 1 mL, 120 °C, 10 h. [b]The yield of *E*-**3a**. [c]The yield of *E*-**3a** and E/Z ratio determined by GC-MS on crude products. [d]At 80 °C. [e]At room temperature.

24% yield of the desired product **3a** (a mixture of *E* and *Z* isomers) using PPh_3 as the reductant (entry 2). After screening different solvents, water proved to be the best option in the transformation (entry 16) due to its high polarity and good solubility of **2a** in water. Lower temperature resulted in poor yield of the product (entries 17, 18). To further improve the results, several surfactants (SDS, CTAB, TX100, Birj35) were employed in the system, but limited success was found, suggesting that the aqueous micelle system may inhibit the ion exchange between substrates and additives and thereby decrease the reaction rate.[16] Various transition metal catalysts ($Pd(OAc)_2$, $PdCl_2$, CuI, $Cu(OAc)_2$) also failed to enhance the yield and selectivity.

With the optimized conditions in hand, a series of terminal alkynes and sodium arenesulfinates were applied in the reaction to establish the scope and generality of this protocol (Table 2). A range of arylethynes which have electron-donating and electron-withdrawing groups reacted with **2a** to give the corresponding adducts *E*-**3a**-**3f** in moderate to excellent yields (entries 1−6). Heteroaryl acetylenes were also applied in the reaction successfully with satisfactory results (entries 7, 8). Likewise, aliphatic terminal alkynes could also provide the desired products under the identical conditions (entries 9−11). In most cases, sodium arenesulfinates afforded the desired products with good yields and selectivity. The reaction was sluggish using sodium arenesulfinates containing strong

Table 2. Iodothiolation of Terminal Alkynes[a]



entry	R	R′	*E*-**3**	yield (%)[b]	E/Z[c]
1	Ph	4-CH_3	*E*-**3a**	82	93/7
2	4-$CH_3C_6H_4$	4-CH_3	*E*-**3b**	85[d]	89/11
3	4-ClC_6H_4	4-CH_3	*E*-**3c**	81	91/9
4	4-$CF_3C_6H_4$	4-CH_3	*E*-**3d**	79	92/8
5	4-*n*-$C_3H_7C_6H_4$	4-CH_3	*E*-**3e**	54	94/6
6	4-BrC_6H_4	4-CH_3	*E*-**3f**	92	97/3
7	3-pyridyl	4-CH_3	*E*-**3g**	90	99/1
8	2-thienyl	4-CH_3	*E*-**3h**	86	99/1
9	cyclopropyl	4-CH_3	*E*-**3i**	36	99/1
10	cyclohexyl	4-CH_3	*E*-**3j**	13[e]	99/1
11	*n*-C_8H_{17}	4-MeO	*E*-**3k**	44	99/1
12	Ph	4-Cl	*E*-**3l**	93[d]	87/13
13	Ph	4-Br	*E*-**3m**	89[d]	87/13
14	Ph	4-O_2N	*E*-**3n**	38[d]	80/20
15	Ph	2-CH_3	*E*-**3o**	78[d]	85/15
16	Ph	4-MeO	*E*-**3p**	74	89/11
17	4-FC_6H_4	4-MeO	*E*-**3q**	84	88/12
18	4-ClC_6H_4	4-MeO	*E*-**3r**	83, 79[f]	90/10
19	4-$MeOC_6H_4$	4-MeO	*E*-**3s**	69	78/22

[a]Reaction conditions: terminal alkynes **1** 0.250 mmol, sodium arenesulfinates **2** 0.375 mmol, iodine 0.375 mmol, PPh_3 0.750 mmol, H_2O 1 mL, 120 °C, 10 h. [b]Isolated yields of *E*-**3**. [c]E/Z ratio determined by GC-MS or ^1H NMR on crude products. [d]Obtained as a mixture of *E* and *Z* stereoisomers. [e]The yield of *E*-**3j** was determined by GC-MS. [f]The reaction scale was 10 mmol.

electron-withdrawing groups such as nitro group (entry 14). In order to show the possibility for large-scale operation, we also scaled up the reaction to 10 mmol, and the reaction proceeded well with 79% yield of the desired product *E*-**3r** (entry 18). Sodium alkylsulfinates failed to produce the desired adducts in the reaction.

To our delight, the protocol was also efficient for the addition of internal alkynes to form the β-iodoalkenyl sulfides (Scheme 1). In all the cases, *E*-isomers were the major products with good yields. To further demonstrate the potential of this methodology, *E*-**4i** was smoothly generated by the addition of sodium *p*-toluenesulfinate and iodine to diphenylacetylene. The product (*E*-**4i**) could be further modified to synthesize (*Z*)-tamoxifen **5a**[7a] that is an estrogen antagonist and effective for metastatic breast cancer.[17] The stereochemistry of *E*-**3a** and *E*-**4a** was determined by comparison of the spectroscopic data for the sulfone *E*-**6a** and *E*-**5b**,[13b,15] which were prepared by oxidation of *E*-**3a** and *E*-**4a**, respectively. The precise configurations were unambiguously confirmed by single-crystal X-ray analysis of *E*-**6a** and *E*-**5b** (Schemes 1 and 2).

Furthermore, the versatile synthetic utility of the iodothiolation adducts was studied, and the results are summarized in Scheme 2. The iodine can be subsequently used in Suzuki and Sonogashira couplings in water at room temperature to afford **6b**, *E*-**6c**.[18] The cyanation of *E*-**3r** could also take place catalyzed by copper.[19] Interestingly, *E*-**3c** was provided through the reaction of *E*-**3r** and *p*-thiocresol under basic conditions by which more β-iodoalkenyl chalcogenides can be prepared. It should be noted that **6e** was generated via hydroxylation and dehydration processes,[20] which may be a robust method for the

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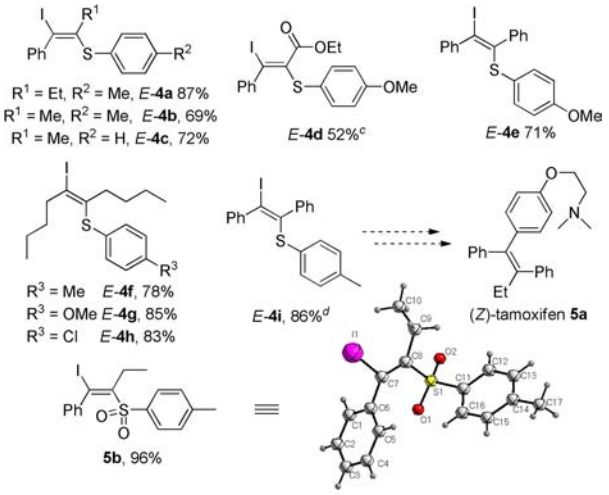
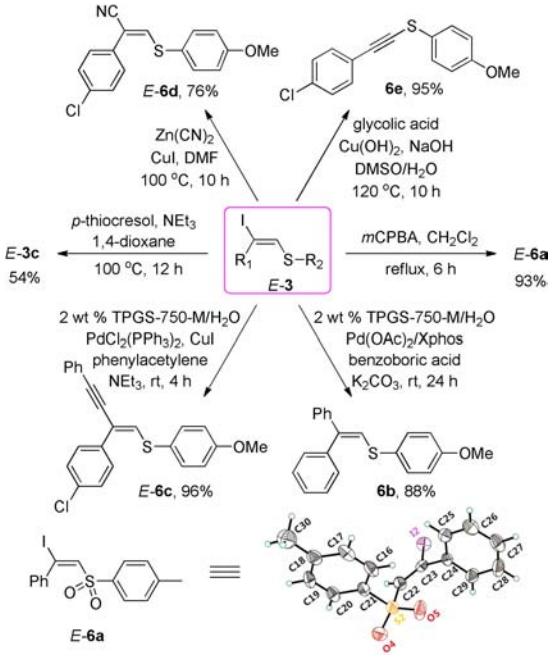
Scheme 1. One-Pot Reactions of Internal Alkynes, Sodium Arenesulfinates, and Iodine[a,b]



[a]Reaction conditions: internal alkynes **1** 0.250 mmol, sodium arenesulfinates **2** 0.375 mmol, iodine 0.375 mmol, PPh_3 0.750 mmol, H_2O 1 mL, 120 °C, 10 h. [b]Isolated yields. [c]10% yield of *Z*-**4d** was formed. [d]The reaction time was 24 h.

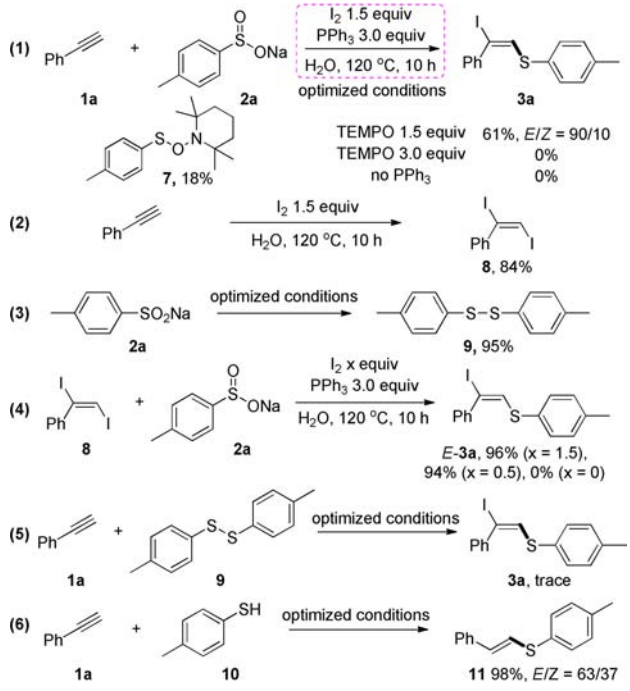
Scheme 2. Transformations of *β*-Iodoalkenyl Sulfides (*E*-3)



synthesis of alkynyl sulfides as versatile and essential building blocks in organic and polymer chemistry.[21]

To further probe the mechanism, control experiments with possible intermediates were designed and investigated (Scheme 3). The reaction was inhibited in the presence of TEMPO (3 equiv), and a 18% yield of **7** was separated and further identified by MS, ^1H, and ^{13}C NMR suggesting the transformation may include a radical process (eq 1). During the reaction, a key intermediate, diiodostyrene **8**, was observed (eq 2). This species can be directly transformed into final product *E*-**3a** in 96% yield under the standard conditions (eq 4), and iodine was necessary for the transformation. Furthermore, disulfide **9** is generated from the **2a** (eq 3), which fail to react

Scheme 3. Mechanistic Studies and Control Experiments



with **1a** to afford **3a** (eq 5). The addition of *p*-thiocresol **10** to **1a** provided **11** as the product instead of **3a** (eq 6). It can be concluded that neither **9** nor **10** is the intermediate of the reaction.

A proposed mechanism for the synthesis of *β*-iodoalkenyl sulfides was illustrated on the basis of these preliminary results (Figure 2). At first, a reduction of sodium arylsulfinate **1**

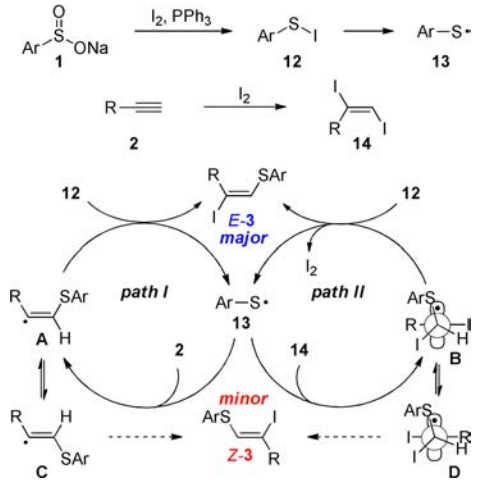


Figure 2. A proposed mechanism for the iodothiolation of alkyne.

mediated by a combination of I_2–PPh_3 leads to arenesulfenyl iodide **12**,[10d,22] which may undergo homolytic cleavage to yield a sulfenyl radical **13**.[23] Meanwhile, diiodovinyl **14** is afforded via an electrophilic addition with perfect stereoselectivity. Hence, there are two plausible paths during the reaction. ***Path I***: **13** adds to the terminal carbon of **2** to form the alkenyl radical **A**. Finally, the radical substitution of **A** with **12** affords the product *E*-**3** and regenerates **13** to complete the radical chain.[6b] ***Path II***: intermediate **B** is derived through the addition of **13** to **14**.

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Then, *E*-**3** is formed by the elimination of iodine radical that further reacts with **12** to produce I_2 and **13**.[24]

In summary, we have developed a one-pot protocol for achieving bifunctionalization of alkyne to produce β-iodoalkenyl sulfides by a radical pathway. The significance of the present chemistry is 3-fold: (1) The research not only reveals a new route for the generation of β-iodoalkenyl sulfides but also offers mechanistic insights into this reaction, which may suggest new processes for the construction of C−S bonds. (2) The procedure is free of foul thiols, organic solvents, and metal catalysts, making it more environmentally friendly and suitable for large-scale operations. (3) The regio- and stereoselective reaction proceeded with high functional group compatibility, which should contribute to the practical synthesis of bioactive complex alkenyl sulfides.

■ ASSOCIATED CONTENT

Supporting Information

Experimental details, crystallographic data of *E*-**6a**, copies of ^{1}H NMR, ^{13}C NMR spectra of all products, and copies of 2D ^{1}H−^{13}C HMBC of *E*-**3p**, *E*-**4d**. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.5b01488.

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Notes

The authors declare no competing financial interest.

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