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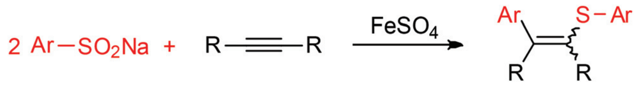
Iron-catalyzed tetrasubstituted alkene formation from alkynes and sodium sulfinates†

Saiwen Liu,[a] Lichang Tang,[a] Hui Chen,[a] Feng Zhao[a] and Guo-Jun Deng*[a,b]

An iron-catalyzed sulfenylation and arylation of alkynes with aryl sulfinic acid sodium salts is described. Various aromatic sodium sulfinates acted both as aryl and sulfenylation reagents, affording tetrasubstituted alkenes in one pot with good yields.

Alkenes are ubiquitous in natural products and biologically active compounds. Many alkenes are also versatile starting materials in the synthesis of functional materials.[1] Various methods have been developed to prepare alkenes, such as the Aldol-type condensation, the Wittig–Horner reaction, olefin metathesis and cross-coupling reactions.[2] Tetrasubstituted alkenes are frequently found in drugs, such as Tamoxifen and Vioxx,[3] and natural products such as Stemona alkaloids and Nileprost analogues.[4] Importantly, tetrasubstituted alkenes also contribute extensively to materials sciences and building blocks for synthetic chemistry.[5] However, the congested nature of the double bond makes it difficult to access these important chemicals efficiently and stereoselectively.[6] Although the McMurry reaction,[7] Wittig olefination or Julia–Kocienski olefination[8] and metathesis[9] can provide different routes for tetrasubstituted alkenes, the efficiency, regio- and stereoselectivity are major problems. The transition-metal-catalyzed cross-coupling reaction of internal alkynes with two different coupling reagents such as aryl halides and aryl boronic acids can provide an alternative synthetic route to tetrasubstituted alkenes.[10] In recent years, the most reliable method to form these compounds is alkyne carbometalation,[11] although there are few other catalytic methods available.[12] Using copper as the catalyst, Gaunt and co-workers successfully employed diaryliodonium triflates as coupling agents to selectively afford all-carbon tetrasubstituted alkenes.[13] Similarly, highly functionalized alkenyl triflates were synthesized *via* electrophilic carbofunctionalization.[14]

As an important class of substituted alkenes, vinyl sulfides are ubiquitous in biologically active compounds and natural products.[15] They can also be used as starting materials to prepare other substituted alkenes *via* C–S bond cleavage.[16] Among the various methods developed, the addition of thiols to alkynes is the most convenient approach to synthesize vinyl sulfides.[17] Transition metals such as rhodium, palladium, actinides and lanthanides and nickel were proved to be efficient catalysts for this kind of reaction. This transformation has also been achieved under transition-metal-free conditions.[18] However, to the best of our knowledge, there were only a few methods developed to synthesize multi-substituted arylvinyl sulfides, especially to triarylvinyl sulfides.[19] Recently, we and others developed various methods for C–C bond formation using stable aromatic sodium sulfinates as aryl sources *via* extrusion of SO_2.[20] This strategy was successfully employed for trisubstituted alkene preparation using palladium as the catalyst.[21] We also developed the iodine-catalyzed regioselective sulfenylation or sulfonylation of indoles using sodium sulfinates as the sulfenylation or sulfonylation reagents.[22] In these reactions, aromatic sodium sulfinates can act as aryl sources and sulfonylation or sulfenylation reagents depending on the reaction conditions. Based on these observations, we envision that it might be possible to synthesize triarylvinyl sulfides in one pot using aromatic sodium sulfinates both as aryl sources and sulfenylation reagents. Herein, we describe an iron-catalyzed tetrasubstituted alkene formation from internal alkynes and two aromatic sodium sulfinates, affording various highly functionalized tetrasubstituted alkenyl sulfides in one pot (Scheme 1).



Scheme 1 Iron-catalyzed arylation and sulfenylation of alkynes.

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[a] *Key Laboratory of Environmentally Friendly Chemistry and Application of Ministry of Education, College of Chemistry, Xiangtan University, Xiangtan 411105, China. E-mail: gjdeng@xtu.edu.cn; Fax: (+86)0731-5829-2251; Tel: (+86)0731-5829-8601*
[b] *Key Laboratory of Molecular Recognition and Function, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080, China*

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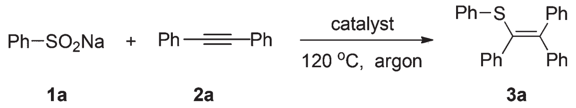
Table 1 Optimization of the reaction conditions[a]

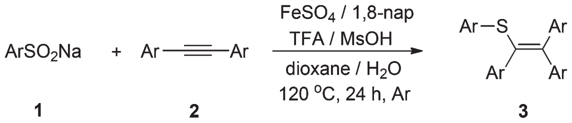


Entry	Catalyst	Ligand	Additive	Solvent	Yield[b] (%)
1			TFA–MsOH	1,4-Dioxane–H_2O	52
2	$FeCl_3·3H_2O$	1,8-naph	TFA–MsOH	1,4-Dioxane–H_2O	77
3	Fe_2O_3	1,8-naph	TFA–MsOH	1,4-Dioxane–H_2O	63
4	$Fe(NO_3)_3$	1,8-naph	TFA–MsOH	1,4-Dioxane–H_2O	69
5	$Fe_2(SO_4)_3$	1,8-naph	TFA–MsOH	1,4-Dioxane–H_2O	73
6	$FeCl_2$	1,8-naph	TFA–MsOH	1,4-Dioxane–H_2O	65
7	Fe(acac)$_3$	1,8-naph	TFA–MsOH	1,4-Dioxane–H_2O	80
8	$FeSO_4·7H_2O$	1,8-naph	TFA–MsOH	1,4-Dioxane–H_2O	90
9	$FeSO_4·7H_2O$	DMAP	TFA–MsOH	1,4-Dioxane–H_2O	59
10	$FeSO_4·7H_2O$	Bipyridine	TFA–MsOH	1,4-Dioxane–H_2O	54
11	$FeSO_4·7H_2O$	DABCO	TFA–MsOH	1,4-Dioxane–H_2O	68
12	$FeSO_4·7H_2O$	1,8-naph	TFA–MsOH	$CH_3CN–H_2O$	73
13	$FeSO_4·7H_2O$	1,8-naph	TFA–MsOH	Anisole–H_2O	55
14	$FeSO_4·7H_2O$	1,8-naph	TFA–MsOH	Diglyme–H_2O	51
15	$FeSO_4·7H_2O$	1,8-naph	TFA–MsOH	DCE–H_2O	74
16	$FeSO_4·7H_2O$	1,8-naph	TFA–MsOH	H_2O	61
17	$FeSO_4·7H_2O$	1,8-naph		1,4-Dioxane–H_2O	Trace

[a] Conditions: **1a** (0.8 mmol), **2a** (0.2 mmol), catalyst (1 mol%), ligand (2 mol%), TFA (0.2 mmol), MsOH (0.2 mmol), solvent (0.3 mL), H_2O (0.1 mL), 120 °C, 24 h under argon unless otherwise noted, 1,8-naph = 1,8-naphthalenediamine. [b] GC yield based on **2a**.

In the first experiment we examined the reaction between sodium benzenesulfinate (**1a**) and diphenylethyne (**2a**) in 1,4-dioxane–water (3 : 1) using trifluoroacetic acid and methanesulfonic acid as additives (Table 1). We were pleased to observe the desired product **3a** in 52% yield without any metal-catalyst under argon at 120 °C (entry 1). Using $FeCl_3·3H_2O$/1,8-naphthalenediamine (1,8-naph) as the catalyst, the yield of **3a** could increase to 77% (entry 2). Furthermore, other iron salts were also investigated for this reaction under similar reaction conditions (entries 3–7). The best result was obtained using $FeSO_4·7H_2O$ as the catalyst (entry 8). Replacing 1,8-naphthalenediamine with other nitrogen-containing ligands led to lower yields (entries 9–11). Solvents screening revealed that dioxane–water (3 : 1) was the most efficient reaction medium (entries 12–15). Notably, the desired product **3a** could be obtained in 61% yield using water as the sole solvent (entry 16). The use of acidic additives is necessary for this kind of transformation, and only trace **3a** was detected in their absence (entry 17). To get satisfactory reaction yield, four equivalents (0.8 mmol) of **1a** were necessary.

Table 2 Vinyl thioether formation from sodium sulfinates and alkynes with the same substituents[a]



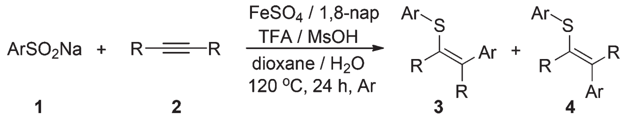
Entry	Ar	Sodium sulfinate	Alkyne	Product	Yield[b] (%)
1[c]	Ph	**1a**	**2a**	**3a**	78
2[c]	4-Me–Ph	**1b**	**2b**	**3b**	72
3	4-Et–Ph	**1c**	**2c**	**3c**	50
4	4-MeO–Ph	**1d**	**2d**	**3d**	48
5	4-F–Ph	**1e**	**2e**	**3e**	70
6	4-Cl–Ph	**1f**	**2f**	**3f**	60

[a] Conditions: **1** (0.8 mmol), **2** (0.2 mmol), $FeSO_4·7H_2O$ (5 mol%), 1,8-naph (10 mol%), TFA (0.2 mmol), MsOH (0.2 mmol), 1,4-dioxane (0.3 mL), H_2O (0.1 mL), 120 °C, 24 h under argon unless otherwise noted. [b] Isolated yield based on **2**. [c] $FeSO_4·7H_2O$ (1 mol%), 1,8-naph (2 mol%).

With the optimized reaction conditions established, we explored the scope and generality of this transformation in the presence of various substituents in aromatic ring. Firstly, we investigated the reaction between aromatic alkynes and arylsulfinic acid sodium salts with the same substituents (Table 2). A slightly lower yield was obtained when a methyl group was presented at the *para* position, and the corresponding product **3b** was obtained in 72% yield (entry 2). Stronger electron-donating groups such as the methoxy group affected the reaction yield significantly (entry 4). Halogen functional groups such as fluoro and chloro were well tolerated under the optimal reaction conditions, and the desired products **3e** and **3f** were obtained in 70% and 60% yield, respectively (entries 5 and 6).

Next, the formation of triarylvinyl sulfides with various substituents in sodium sulfinates and internal alkynes was explored in this reaction and the results are summarized in Table 3. The reactions with sulfinic acid sodium salts bearing electron-donating (entries 1–3) and electron-withdrawing substituents (entries 4 and 6) at the aromatic ring proceeded smoothly to give the desired products in moderate to good yields. Common functional groups, including fluoro

Table 3 Vinyl thioether formation from sodium sulfinates and alkynes[a]

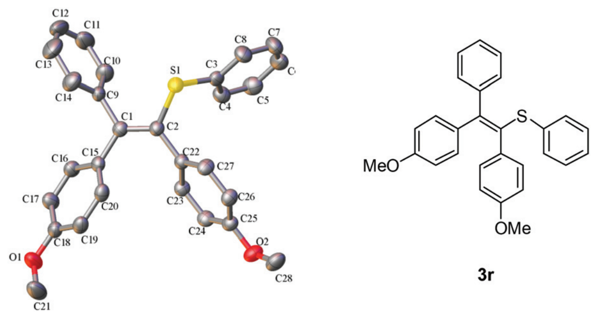


Entry	Sodium sulfinate **1**	Alkyne **2**	Product	Yield[b] (%)
	Ar =	R =		
1[c]	4-Me–Ph **1b**	Ph **2a**	**3g** + **4g**	74 (1.2 : 1)
2	4-Isopropyl-Ph **1g**	Ph **2a**	**3h** + **4h**	50 (1.2 : 1)
3	4-MeO–Ph **1d**	Ph **2a**	**3i** + **4i**	67 (1 : 1)
4[c]	4-CF$_3$–Ph **1h**	4-Me–Ph **2b**	**3j** + **4j**	62 (1 : 1)
5	4-OCF$_3$–Ph **1i**	4-Me–Ph **2b**	**3k** + **4k**	70 (1 : 1)
6	4-F–Ph **1e**	4-Me–Ph **2b**	**3l** + **4l**	68 (1 : 1)
7[c]	4-Cl–Ph **1f**	4-Me–Ph **2b**	**3m** + **4m**	70 (1 : 1)
8[c]	4-Br–Ph **1j**	4-Me–Ph **2b**	**3n** + **4n**	72 (1 : 1)
9	4-CN–Ph **1k**	Ph **2a**	**3o** + **4o**	65 (1 : 1)
10	Ph **1a**	4-Me–Ph **2b**	**3p** + **4p**	71 (1 : 1)
11	Ph **1a**	4-Ethyl-Ph **2c**	**3q** + **4q**	73 (1 : 1.1)
12	Ph **1a**	4-MeO–Ph **2d**	**3r** + **4r**	68 (1 : 1)
13	4-Me–Ph **1b**	4-F–Ph **2e**	**3s** + **4s**	72 (1 : 1)
14	4-Me–Ph **1b**	4-Cl–Ph **2f**	**3t** + **4t**	78 (1 : 1)
15	4-Me–Ph **1b**	2-Thienyl **2g**	**3u** + **4u**	51 (1 : 1.5)
16	Ph **1a**	*n*-Propyl **2h**	**3v** + **4v**	20 (1 : 1)

[a] Conditions: **1** (0.8 mmol), **2** (0.2 mmol), FeSO$_4$·7H$_2$O (5 mol%), 1,8-naph (10 mol%), TFA (0.2 mmol), MsOH (0.2 mmol), 1,4-dioxane (0.3 mL), H$_2$O (0.1 mL), 120 °C, 24 h under argon unless otherwise noted. [b] Isolated yield based on **2**, ratios were determined by NMR. [c] FeSO$_4$·7H$_2$O (1 mol%), 1,8-naph (2 mol%).

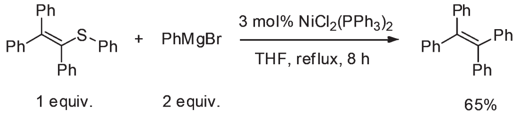
(entries 4–6, 13), chloro (entries 7 and 14) and bromo (entry 8) were all compatible with this catalytic reaction. Sodium sulfinates with strong electron-withdrawing groups such as cyano also smoothly coupled with **2a**, and gave **3o** and **4o** in 65% yield (entry 9). It is noteworthy that hetero 1,2-di(thiophen-2-yl)ethyne (**2g**) also participated in the reaction to afford the corresponding products **3u** and **4u** in 51% total yield (entry 15). In addition, the reaction of **1a** with aliphatic alkyne oct-4-yne **2h** afforded the desired product in 20% yield (entry 16). In most cases, a mixture of two isomers (near 1 : 1 ratio) was obtained which is difficult to separate. Isomer **3r** was successfully separated from **4r**, and the structure of **3r** is confirmed by X-ray crystallography (Fig. 1). The exact reaction mechanism is not clear at this stage since it is hard to trap some key intermediates during the reaction process.[23]

Independently, Takei and co-workers showed that alkenyl and aryl sulfides can be coupled with Grignard reagents in the presence of [NiCl$_2$(PPh$_3$)$_2$] catalyst (3 mol%).[24] When phenyl-(1,2,2-triphenylvinyl)sulfane **3a** was treated with phenylmagnesium bromide, the desired product was obtained in 65% isolated yield (Scheme 2).



3r

Fig. 1 X-ray structure of **3r**.



Scheme 2 Synthetic application.

In summary, we have developed an iron-catalyzed addition of aromatic sodium sulfinates to internal alkynes. Aromatic sodium sulfinates acted both as aryl sources and sulfenylation reagents. The C–C and C–S bond forming reactions were realized in one pot using iron as an environmentally benign catalyst. Acid was found to be crucial for the formation of tetrasubstituted alkenes. Although the stereoselectivity is not satisfactory at this stage, this novel process can provide an efficient approach to triarylvinyl sulfides. The mechanism, selectivity and synthetic application of this transformation are under investigation.

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23 Treatment of (1,2-diphenylvinyl)(phenyl)sulfane or ethene-1,1,2-triyltribenzene which is thought to be the possible intermediate with the standard reaction conditions did not lead to the final desired product **3a**. Addition of 1.5 equiv. of TEMPO (2,2,6,6-tetramethylpiperidinooxy) completely inhibited the reaction. Based on these observations, we guess it might be a concerted radical reaction, and the arylation and sulfenylation reaction occur at the same time.

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