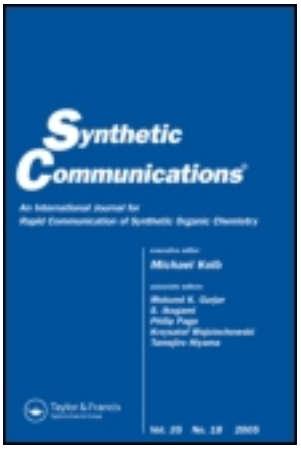

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An Improved Synthesis of Vinyl- and β-Iodovinyl Sulfones by a Molecular Iodine-Mediated One-Pot Iodosulfonation-Dehydroiodination Reaction

Tassaporn Sawangphon [a], Praewpan Katrun [a], Korbua Chaisiwamongkhol [a], Manat Pohmakotr [a], Vichai Reutrakul [a], Thaworn Jaipetch [b], Darunee Soorukram [a] & Chutima Kuhakarn [a]

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AN IMPROVED SYNTHESIS OF VINYL- AND β-IODOVINYL SULFONES BY A MOLECULAR IODINE-MEDIATED ONE-POT IODOSULFONATION-DEHYDROIODINATION REACTION

Tassaporn Sawangphon,[1] Praewpan Katrun,[1] Korbua Chaisiwamongkhol,[1] Manat Pohmakotr,[1] Vichai Reutrakul,[1] Thaworn Jaipetch,[2] Darunee Soorukram,[1] and Chutima Kuhakarn[1]

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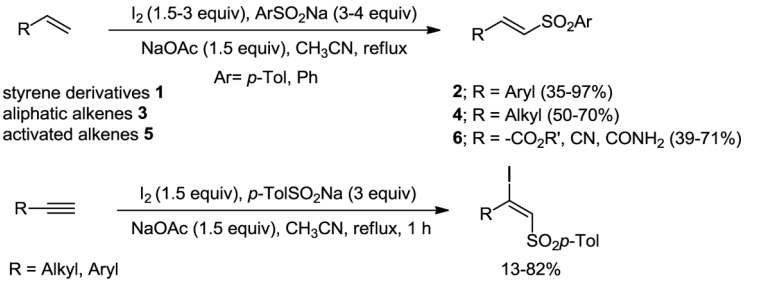
GRAPHICAL ABSTRACT



Abstract *An improved one-pot method to synthesize vinyl sulfones from unsaturated systems by using molecular iodine/sodium arenesulfinate/sodium acetate as reagents was described. Vinyl sulfones derived from styrene derivatives were generally obtained in good to excellent yields except for those bearing strong electron releasing substituent. Aliphatic alkenes and activated alkenes gave the corresponding vinyl sulfone products in moderate to good yields. Arylacetylenes yielded the respective β-iodovinyl sulfones in good yields while low yield was observed with aliphatic terminal alkyne. The potentials of the method entail simplicity, short reaction time, non-anhydrous reaction conditions, employing inexpensive, non-metallic reagent and integrating two reactions that are commonly accomplished separately into a single operation.*

Supplemental materials are available for this article. Go to the publisher's online edition of Synthetic Communications® *to view the free supplemental file.*

Keywords Alkenes; alkynes; iodine; sulfur; vinyl sulfones

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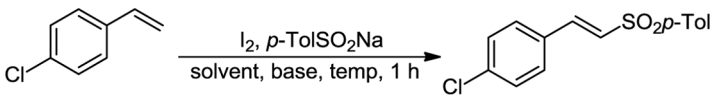
INTRODUCTION

Sulfones have gained much attention in both organic synthesis and medicinal chemistry because of their wide versatility as synthetic intermediates and interesting biological activities.[1] In particular, vinyl sulfones are important moieties found in various biologically active compounds[2] and useful synthetic synthons in organic synthesis.[3] As a result, there are numerous efforts aiming at developing efficient and mild methods for the synthesis of vinyl sulfones.[4] The most recent ones include Ir(II)-catalyzed allylic substitution of allyl sulfinate and isomerization,[5a] copper-catalyzed or $NaIO_4$/KI/AcOH-mediated oxidation of sodium sulfinates,[5b,c] and $Pd(OAc)_2$-catalyzed conjugate addition.[5d] Recently, we reported synthesis of vinyl sulfones and β-iodovinyl sulfones by the reaction of aryl sulfinate with alkenes and alkynes using a combination of $PhI(OAc)_2$/KI as reagents.[6] In the course of our study, we found that vinyl sulfones can be obtained in one pot by using molecular iodine and sodium arenesulfinate as reagents in the presence of an external base. Although a similar process has been previously reported,[4f–i] the reaction required two steps and lengthy reaction time on some substrates and had modest substrate scope. Even though Nájera et al. later employed sodium toluenesulfinate tetrahydrate and iodine in methanol followed by treatment with alcoholic potassium hydroxide for the conversion of styrene to (*E*)-β-tosylstyrene in one pot, detailed study on substrate scope was not conducted.[4j] In recent years, many reactions have been reported using iodine as promoter or catalyst.[7] In view of the importance of vinyl sulfones and molecular iodine as economical reagent, we now report an improved and convenient experimental procedure to synthesize vinyl sulfones and β-iodovinyl sulfones from alkenes and alkynes by molecular iodine–mediated one-pot iodosulfonation followed by base-induced dehydroiodination reaction.

RESULTS AND DISCUSSION

Initially, a reaction of 4-chlorostyrene and sodium *p*-toluenesulfinate was investigated. Based on our previous study, acetonitrile was primarily chosen as a solvent for the reaction.[6] When a mixture of 4-chlorostyrene (**1a**) and sodium *p*-toluenesulfinate (3 equiv), iodine (1.5 equiv) and sodium acetate (1.5 equiv) was stirred at room temperature for 1 h, the expected vinyl sulfone (**2a**) was obtained in 71% isolated yield (Table 1, entry 1). When dichloromethane was employed as the solvent, ^{1}H-NMR of a crude product indicated that it was a mixture of β-iodosulfone and vinyl sulfone (Table 1, entry 2). Elimination of HI to yield vinyl sulfone readily took place during purification by silica gel-column chromatography to yield **2a** in 85% yield. However, the product obtained slowly turned brown upon standing at room temperature and its TLC characteristics showed additional spots. This also happened when ethyl acetate was used as the solvent (Table 1, entry 3). When the reaction was performed in refluxing acetonitrile, the production of **2a** was increased to 90% yield (Table 1, entry 4). At refluxing temperature, other organic solvents including ethanol, tetrahydrofuran, ethyl acetate, toluene, and chloroform gave inferior results (Table 1, entries 5–9). It should also mention that moderate yield (50%) of **2a** was obtained when water was used as the solvent (Table 1, entry 10). Additionally, when sodium *p*-toluenesulfinate was employed in

Table 1. Investigation of optimized reaction conditions[a]



1a **2a**

Entry	Base	Solvent	Temp. (°C)	Yield (%)
1	NaOAc	CH_3CN	Rt	71
2	NaOAc	CH_2Cl_2	Rt	85
3	NaOAc	EtOAc	Rt	80
4	NaOAc	CH_3CN	Reflux	90
5	NaOAc	EtOH	Reflux	81
6	NaOAc	THF	Reflux	80
7	NaOAc	EtOAc	Reflux	78
8	NaOAc	Toluene	Reflux	72
9	NaOAc	$CHCl_3$	Reflux	11
10	NaOAc	H_2O	Reflux	50
11	DBU	CH_3CN	Reflux	65
12	NEt_3	CH_3CN	Reflux	87
13	$NaHCO_3$	CH_3CN	Reflux	77
14	Na_2CO_3	CH_3CN	Reflux	80
15	K_2CO_3	CH_3CN	Reflux	83

[a]All reactions were performed using 4-chlorostyrene (0.5 mmol), iodine (1.5 equiv), *p*-$TolSO_2Na$ (3.0 equiv), and base (1.5 equiv).

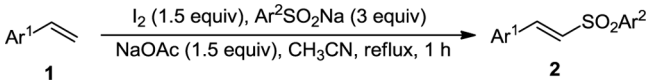
lesser amount, lower yields were obtained. The choice of base was also briefly screened and the results are shown in Table 1 (entries 11–15).

Even though triethylamine (TEA) gave comparable results to those when sodium acetate was employed as the base, the crude mixture was not clean, as shown by its TLC characteristics. Based on the results shown in Table 1, the standard reaction conditions are to use iodine (1.5 equiv), and sodium *p*-toluenesulfinate (3 equiv), sodium acetate (1.5 equiv) in acetonitrile and bring the reaction mixture to reflux for 1 h. The synthetic utilities of the method were demonstrated by further exploration of compatibility of different substrates (i.e., styrene derivatives, aliphatic alkenes, activated alkenes, and alkynes). The results are summarized in Tables 2–5.

When structurally different styrene derivatives were exposed to the standard reaction conditions, in most cases, the corresponding vinyl sulfone products were obtained in good yields except for those substituted with electron-releasing substituents, in which case poor to moderate yields were obtained (Table 2). In case of 4-methoxystyrene, the competing reaction was the methoxy-assisted elimination of iodine followed by addition of sodium *p*-toluenesulfinate to yield compound **2i′** (Scheme 1).

2- and 4-vinylpyridines (**1m** and **n**) also underwent the reaction to yield the corresponding vinyl sulfone products in good yields while α-methylstyrene (**1o**) led to a mixture of allyl sulfone and *E*-vinyl sulfone (see Supporting Information, available online, for nuclear Overhauser effect data of **2o**) with the allyl sulfone being a major product (Scheme 2). Efforts toward optimization to obtain vinyl sulfone **2o** as a major product were not successful. It is worth mentioning that when either

Table 2. Synthesis of vinyl sulfones derived from styrene derivatives[a]



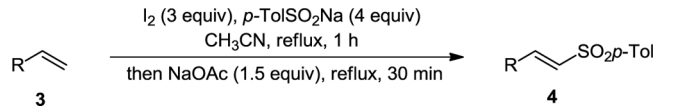
Entry	Alkene **1**	Ar^1	Ar^2	Product **2** (% yield)[b]
1	**1a**	4-ClC_6H_4	*p*-Tol	**2a**(90)
2	**1b**	3-ClC_6H_4	*p*-Tol	**2b**(93)
3	**1c**	2-ClC_6H_4	*p*-Tol	**2c** (86)
4	**1d**	4-BrC_6H_4	*p*-Tol	**2d** (87)
5	**1e**	3-FC_6H_4	*p*-Tol	**2e** (93)
6	**1f**	3-$O_2NC_6H_4$	*p*-Tol	**2f** (95)
7	**1g**	C_6H_5	*p*-Tol	**2g** (80)
8	**1h**	4-$CH_3C_6H_4$	*p*-Tol	**2h** (70)
9	**1i**	4-$CH_3OC_6H_4$	*p*-Tol	**2i** (35)[c]
10	**1j**	4-$AcOC_6H_4$	*p*-Tol	**2j** (91)
11	**1k**	3-$OHCC_6H_4$	*p*-Tol	**2k** (97)
12	**1l**	4-$(ClCH_2)C_6H_4$	*p*-Tol	**2l** (85)[Ar^1 = 4-(*p*-$TolSO_2CH_2)C_6H_4$]
13	**1a**	4-ClC_6H_4	Ph	**2aa** (80)
14	**1b**	3-ClC_6H_4	Ph	**2bb** (92)
15	**1c**	2-ClC_6H_4	Ph	**2cc** (84)
16	**1d**	4-BrC_6H_4	Ph	**2dd** (87)
17	**1f**	3-$O_2NC_6H_4$	Ph	**2ff** (93)
18	**1g**	C_6H_5	Ph	**2gg** (78)
19	**1l**	4-$(ClCH_2)C_6H_4$	Ph	**2ll** (90)[Ar^1 = 4-$(PhSO_2CH_2)C_6H_4$]

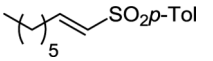
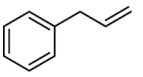
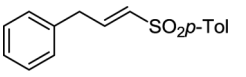
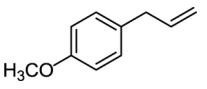
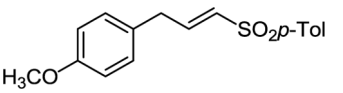
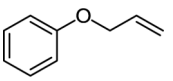
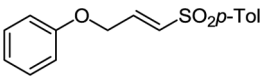
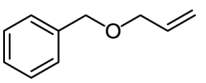
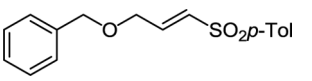
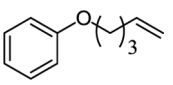
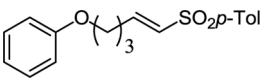
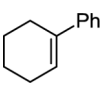
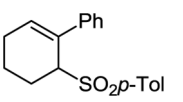
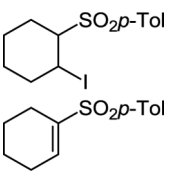
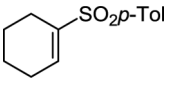
[a]All reactions were performed using styrene derivative (0.5 mmol).
[b]Isolated yields.
[c]Product **2i′** was obtained in 33%.

compound **2o** or **2o′** was treated with an excess amount of organic bases (i.e., Et_3N and DBU), an approximately 1:5 mixture of **2o:2o′** was obtained (^{1}H NMR monitoring).

In the case of aliphatic alkenes, 1-octene under standard reaction conditions gave a mixture of the corresponding vinyl sulfone and β-iodosulfone as shown by ^{1}HNMR (300 MHz), and only 37% yield of vinyl sulfone product was isolated after purification. Thus, attempts to examine suitable reaction conditions were carried out. After an extensive investigation, it was found that the reaction with 1-octene required an excess amount of both iodine (3 equiv) and sodium arenesulfinate (4 equiv) in refluxing acetonitrile for 1 h followed by addition of sodium acetate (1.5 equiv), and vinyl sulfone derived from 1-octene was obtained in 70% isolated yield. It is worth mentioning that lower yield (31%) was observed if sodium acetate was added at the beginning of the reaction. Having established optimized reaction conditions, we then subjected a collection of aliphatic alkenes to the reaction conditions, and the results are summarized in Table 3. The corresponding vinyl sulfones were obtained in moderate to good yields. It should also be emphasized that no isomerization to allylic sulfones were observed for vinyl sulfones **4b, 4c**, and **4d**. Even though 1-phenylcyclohexene (**3g**) gave allylic sulfone **4g** in moderate yield (61%), cyclohexene (**3h**), in contrast, gave a mixture of β-iodosulfone adduct **4h′** (24%)

Table 3. Synthesis of vinyl sulfones derived from aliphatic alkenes[a]



Entry	Alkene		Product		Yield (%)[b]
1		**3a**		**4a**	70 (38)[d]
2		**3b**		**4b**	55
3		**3c**		**4c**	55
4		**3d**		**4d**	58
5		**3e**		**4e**	50
6		**3f**		**4f**	67
7		**3g**		**4g**	61
8		**3h**		**4h′ 4h**	24 12
9[c]		**3h**		**4h**	55

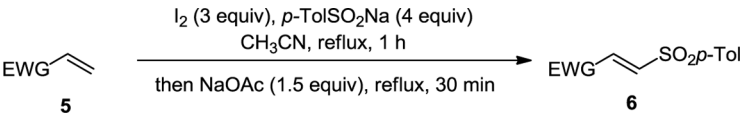
[a]All reactions were performed by using alkene (0.5 mmol).

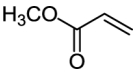
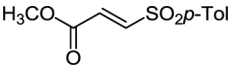
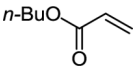
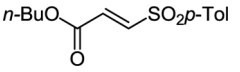
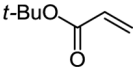
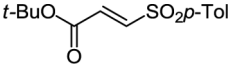
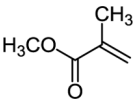
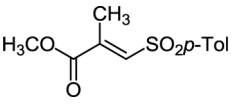
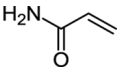
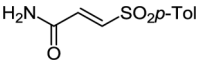
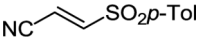
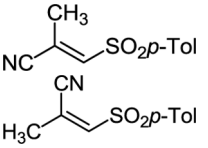
[b]Isolated yields.

[c](1) *p*-TolSO_2Na and I_2 were premixed in acetonitrile (15 min) before cyclohexene (0.5 mmol) in acetonitrile was added, reflux, 1 h then NaOAc (1.5 equiv), reflux, 30 min; (2) DBU (1.5 equiv, acetonitrile, rt, 30 min.

[d]The reaction of 1-octene (**3a**) with iodine in methanol followed by treatment with methanolic potassium hydroxide gave the corresponding vinyl sulfone in 38% yield.

Table 4. Synthesis of vinyl sulfonesderived from activated alkenes[a]



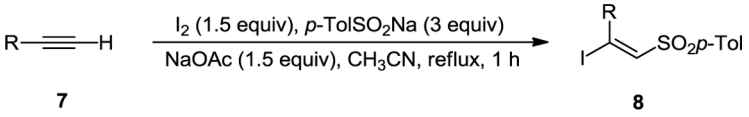
Entry	Substrate		Product		Yield (%)[b]
1		**5a**		**6a**	59
2		**5b**		**6b**	70 (nd)[c]
3		**5c**		**6c**	65
4		**5d**		**6d**	71
5		**5e**		**6e**	53
6		**5f**		**6f**	39
7		**5g**		**6ga** (*E*-isomer) **6gb** (*Z*-isomer)	10 33

[a]All reactions were performed by using activated alkene (0.5 mmol).
[b]Isolated yields.
[c]The reaction of *n*-butyl acrylate (**5a**) with iodine in methanol followed by treatment with methanolic potassium hydroxide failed to provide the corresponding vinyl sulfone.

and vinyl sulfone **4h** (12%) under similar reaction conditions (entries 7 and 8). Gratifyingly, moderate yield (55%) of vinyl sulfone derived from cyclohexene was obtained by premixing the sulfinate salt with iodine before cyclohexene was introduced followed by a separated DBU-induced HI elimination step (entry 9).

Under similar reaction conditions to those used for aliphatic alkenes, activated alkenes afforded the corresponding vinyl sulfones in variable yields, and the results are summarized in Table 4. Moderate yields (53–71%) were obtained when α,β-unsaturated alkyl esters and amide were employed as precursors (Table 4, entries 1–5). α,β-Unsaturated nitriles gave the corresponding vinyl sulfones in poor yield (entry 6); methacrylonitrile gave a mixture of two geometrical isomers with the *Z*-isomer being a major isomer (entry 7). The stereochemistry assigned for vinyl

Table 5. Synthesis of β-iodovinylsulfones derived from alkynes[a]



7 **8**

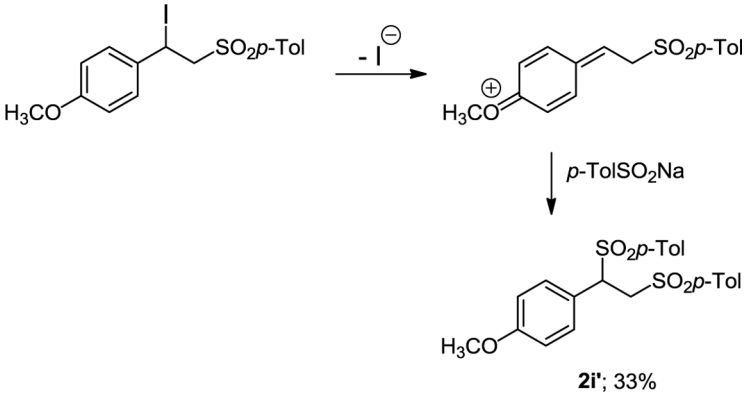
Entry	Alkyne **7**	R	Product **8** (% yield)[b]
1	**7a**	C_6H_5	**8a** (74)
2	**7b**	4-$O_2NC_6H_4$	**8b** (79)
3	**7c**	4-$CH_3C_6H_4$	**8c** (82)
4	**7d**	4-$CH_3OC_6H_4$	**8d** (82)
5	**7e**	$CH_3(CH_2)_5$	**8e** (13)

[a]All reactions were performed using alkyne (0.5 mmol).
[b]Isolated yields.

sulfones **6d**, **6ga**, and **6gb** was based on their NOE experiments (see Supporting Information).

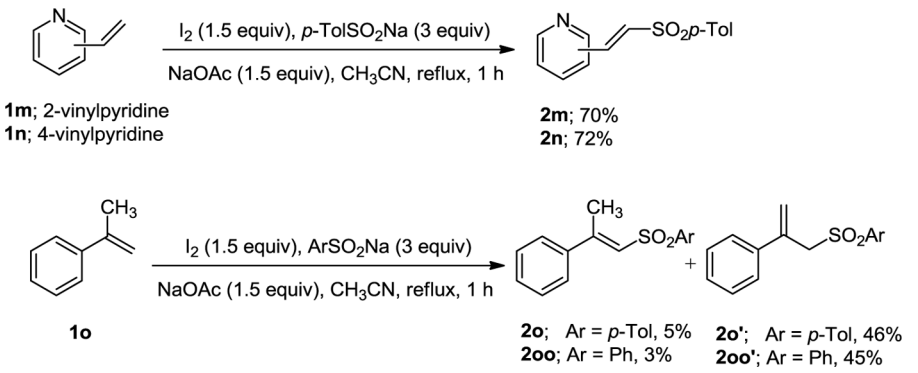
Because of the importance of β-halovinyl sulfones as synthetic intermediates in organic synthesis,[8] our efforts also extended to the synthesis of β-iodovinyl sulfones starting from the alkyne substrates. Under the reaction conditions used for styrene derivatives, the corresponding β-iodovinyl sulfones derived from phenylacetylene derivatives were obtained in acceptable yields (Table 5, entries 1–4) while poor yield was observed with that derived from aliphatic alkyne (Table 5, entry 5). The stereochemistry of **8e** was assigned by its NOE experiments (see Supporting Information) and was confirmed to be *E* isomer. The stereochemistry of compounds **8a**–**d** was then assigned on the basis of that of **8e**.

Finally, similar to the previous works, the reaction was believed to mechanistically proceed via radical pathway and the mechanism for the reaction is shown in Scheme 3.[4f–k] Sodium arenesulfinate reacts with iodine to give arenesulfonyl iodide, which undergoes homolytic cleavage under refluxing acetonitrile to yield an arenesulfonyl radical. Addition of the sulfonyl radical to olefin takes place chemoselectively



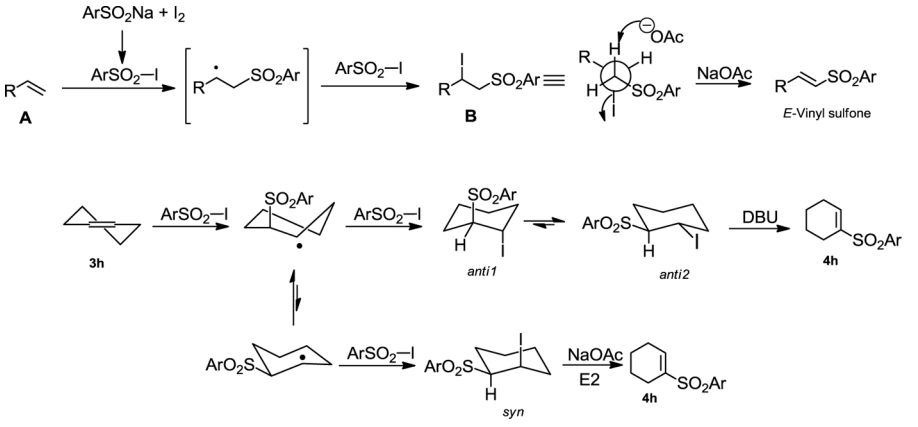
2i'; 33%

Scheme 1. Formation of compound **2i'**.



Scheme 2. Reaction of vinylpyridiens **1m** and **n** and α-methylstyrene (**1o**).

to form a more stabilized carbon radical. Subsequent abstraction with iodine from arenesulfonyl iodide affords β-iodosulfone, which yields vinyl sulfone after base-promoted elimination of HI. In the case of cyclohexene, under standard reaction conditions, the corresponding β-iodosulfone adducts most likely from the *syn* isomer where both the hydrogen and the iodo groups are in antiperiplanar position readily undergoes elimination of HI (via an E2 mechanism). For the *anti* isomer, elimination of HI by the action of NaOAc via an E2 mechanism would lead to allyl sulfone as a product. However, the allyl sulfone was not isolated from this reaction. Therefore, for the reaction of cyclohexene without treatment with DBU, a mixture of vinyl sulfone and β-iodovinyl sulfone was obtained. Vinyl sulfone can be obtained after treatment of the crude mixture containing both β-iodosulfone and vinyl sulfone with strong base (DBU). Because of the higher acidity of H neighboring to the sulfonyl group, DBU-mediated HI elimination yielded vinyl sulfone **4h** as a product. It is also believed that the iodosulfonation of 1-phenylcyclohexene proceeds in a similar fashion but the corresponding β-iodosulfone adducts readily undergoes HI elimination under the reaction conditions to yield allyl sulfone as the product.



Scheme 3. Mechanistic pathway.

CONCLUSION

We described an improved method for the synthesis of vinyl sulfones derived from various types of unsaturated system by using molecular iodine and sodium arenesulfinate as reagents in the presence of an external base. The reaction integrates two reactions into a single operation and was found to be suitable for a variety of substrates. In view of the efficiency of the method, the present approach is direct, convenient, and time efficient.

EXPERIMENTAL

All known compounds were characterized by ^{1}H and ^{13}C NMR, infrared (IR), and mass spectroscopy, and their spectroscopic data were identical to those reported in the literature: **2a**, **2f**, **2h**, **2o**, **2o′**, **2aa**, **2gg**, **2oo**, **2oo′**, **6a**;[9] **2b**;[10] **2c**, **2j**, **8a**, **8c–8e**;[4l] **2d**, **2cc**, **4c**, **4f**, **6b–6d**, **8b**;[6] **2g**, **4g**, **4h**;[4f] **2i**;[11] **2m**, **2n**;[12] **2ff**;[13] **2dd**;[4v] **4a**;[4k] **4b**;[14] **4d**;[15] **4e**;[16] and **6f**.[4y] All new compounds were characterized by ^{1}H and ^{13}C NMR, IR, and high-resolution mass spectroscopy (HRMS). ^{1}H and ^{13}C NMR spectra were run on Bruker DPX-300 and Bruker Avance 500 spectrometers in $CDCl_3$ and acetone-d_6. IR spectroscopy was carried out on a Perkin-Elmer GX FT-IR system spectrometer, HRMS was carried out on a Bruker micro TOF spectrometer, the elemental analysis was performed on a Perkin-Elmer elemental analyzer 2400 CHN, and melting points (uncorrected) were determined on an Electrothermal IA 9000 apparatus and Gallenkamp apparatus.

General Procedure A

I_2 (190.4 mg, 0.75 mmol) was added to a suspension mixture of styrene derivative (or alkyne) (0.5 mmol), sodium arenesulfinate (1.5 mmol), and NaOAc (61.5 mg, 0.75 mmol) in CH_3CN (2 mL), and the reaction mixture was vigorously stirred at refluxing temperature for 1 h. Upon completion of the reaction, the reaction mixture was quenched by the addition of saturated aqueous sodium thiosulfate ($Na_2S_2O_3$) (5 mL) and basified with saturated aqueous sodium hydrogen carbonate ($NaHCO_3$) (5 mL). Further stirring was followed by extraction with ethyl acetate (3×15 mL). The combined organic extracts were washed with water (20 mL) and brine (20 mL), dried (anhydrous $MgSO_4$), filtered, and concentrated (aspirator). The residue was purified by column chromatography (silica gel) to furnish the analytically pure product, and all solids were recrystallized from hexanes/CH_2Cl_2.

(*E*)-1-Chloro-4-(2-tosylvinyl)benzene (2a). White solid. Mp: 148–149 °C (lit.[9] 151–152 °C); $R_f = 0.23$ (hexanes–EtOAc, 8.5:1.5). IR (KBr): 3055 (aromatic), 1613 (C=C), 1592, 1489 and 1450 (aromatic), 1304 and 1143 (SO_2). ^{1}H NMR (300 MHz, $CDC1_3$): $\delta = 7.75$ (d, $J = 8.0$ Hz, 2H), 7.53 (d, $J = 15.4$ Hz, 1H), 7.35–7.26 (m, 6H), 6.76 (d, $J = 15.4$ Hz, 1H), 2.36 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 144.5$, 140.4, 137.6, 137.1, 131.0, 130.0, 129.6, 129.3, 128.3, 127.7, 21.6. HRMS (ESI-TOF): m/z [M + Na^+] calcd. for $C_{15}H_{13}ClO_2SNa$: 315.0222; found: 315.0214.

(*E*)-1-Chloro-4-[2-(phenylsulfonyl)vinyl]benzene (2aa). White solid. Mp: 128–131 °C (lit.[9] 133–134 °C); $R_f = 0.15$ (hexanes–EtOAc, 9:1). IR (KBr): 3050 (aromatic), 1616 (C=C), 1586, 1486 and 1447 (aromatic), 1309 and 1149 (SO_2). ^{1}H NMR (300 MHz, $CDC1_3$): $\delta = 7.96$ (d, $J = 7.3$ Hz, 2H), 7.67–7.53 (m, 4H), 7.43–7.33 (m, 4H), 6.89 (d, $J = 15.5$ Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 140.9$, 140.5, 137.2, 133.5, 130.9, 129.7, 129.4, 128.0, 127.7. HRMS (ESI-TOF): m/z [M + Na$^+$] calcd. for $C_{14}H_{11}ClO_2SNa$: 301.0066; found: 301.0042.

(*E*)-1-Chloro-3-[2-(phenylsulfonyl)vinyl]benzene (2bb). White solid. Mp: 98–100 °C; $R_f = 0.30$ (hexanes–EtOAc, 8.5:1.5). IR (KBr): 3048 (aromatic), 1618 (C=C), 1565, 1479 and 1448 (aromatic), 1300 and 1145 (SO_2). ^{1}H NMR (500 MHz, $CDC1_3$): $\delta = 7.97$ (d, $J = 8.2$ Hz, 2H), 7.68–7.62 (m, 2H), 7.60–7.57 (m, 2H), 7.48 (s, 1H), 7.41–7.33 (m, 3H), 6.91 (d, $J = 15.4$ Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 140.7$, 140.4, 135.1, 134.2, 133.5, 131.0, 130.3, 129.4, 129.0, 128.1, 127.7, 126.8. HRMS (ESI-TOF): m/z [M + Na$^+$] calcd. for $C_{14}H_{11}ClO_2SNa$: 301.0075; found: 301.0042.

(*E*)-1-Fluoro-3-(2-tosylvinyl)benzene (2e). White solid. Mp: 75–78 °C; $R_f = 0.50$ (hexanes–EtOAc, 4:1). IR (KBr,): 3053 (aromatic), 1617 (C=C), 1600 and 1509 (aromatic), 1304 and 1142 (SO_2). ^{1}H NMR (300 MHz, $CDC1_3$): $\delta = 7.84$ (d, $J = 8.4$ Hz, 2H) 7.62 (d, $J = 15.4$ Hz, 1H), 7.41–7.31 (m, 3H), 7.27 (d, $J = 8.3$ Hz, Hz, 1H), 7.20-7.08 (m, 2H), 6.88 (d, $J = 15.4$ Hz, 1H), 2.45 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 162.9$, 144.6, 140.3, 137.3, 134.6, 130.6, 130.0, 129.1, 127.7, 124.5, 117.9, 114.7, 21.6. HRMS (ESI-TOF): m/z [M + Na$^+$] calcd for $C_{15}H_{13}FO_2SNa$: 299.0518; found: 299.0473.

(*E*)-1-Methoxy-4-(2-tosylvinyl)benzene (2i). White solid. Mp: 177–180 °C (lit.[11] 178–180 °C); $R_f = 0.28$ (hexanes–EtOAc, 4:1). IR (KBr): 3053 (aromatic), 1601 (C=C), 1510 and 1464 (aromatic), 1303 and 1141 (SO_2), 1258 and 1087 (C-O). ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.82$ (d, $J = 8.0$ Hz, 2H), 7.60 (d, $J = 15.4$ Hz, Hz, 1H), 7.42 (d, $J = 8.6$, 2H), 7.33 (d, $J = 8.0$ Hz, 2H), 6.89 (d, $J = 8.7$ Hz, 2H), 6.71 (d, $J = 15.4$ Hz, 1H), 3.85 (s, 3H), 2.44 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 162.0$, 144.1, 141.7, 138.2, 130.3, 129.9, 127.5, 125.1, 124.9, 114.5, 55.4, 21.5. HRMS (ESI-TOF): m/z [M + Na$^+$] calcd for $C_{16}H_{16}O_3SNa$: 311.0718; found: 311.0706.

4,4′-(1-(4-Methoxyphenyl)-ethane-1,2-diyldisulfonyl)bis-(methylbenzene) (2i′). White solid. Mp: 124–125 °C; $R_f = 0.14$ (hexanes–EtOAc, 4:1). IR (KBr): 2976 and 2923 (C-H of aromatic), 1597, 1516, and 1453 (aromatic), 1305 and 1136 (SO_2), 1251 and 1082 (C-O). ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.44$ (d, $J = 8.3$ Hz, 2H), 7.39 (d, $J = 8.3$ Hz, 2H), 7.21 (d, $J = 8.5$, 2H), 7.14 (d, $J = 8.5$ Hz, 2H), 6.86 (d, $J = 8.8$ Hz, 2H), 6.61 (d, $J = 8.8$ Hz, 2H), 4.55 (dd, $J = 12.0$, 2.5 Hz, 1H), 4.11 (dd, $J = 14.3$, 2.5 Hz, 1H), 3.91 (dd, $J = 14.3$, 12.0 Hz, 1H), 3.77 (s, 3H), 2.42 (s, 3H), 2.39 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 160.2$, 145.1, 144.5, 136.2, 133.1, 131.0, 129.5, 129.1, 127.8, 121.0, 113.7, 65.6, 55.1, 54.0, 21.5, 21.4. HRMS (ESI-TOF): m/z [M + Na$^+$] calcd for $C_{23}H_{24}O_5S_2Na$: 467.0963; found: 467.1028.

(*E*)-3-(2-Tosylvinyl)benzaldehyde (2k). White solid. Mp: 137–140 °C; $R_f = 0.18$ (hexanes–EtOAc, 7:3). IR (KBr): 3049 (aromatic), 2927 (aliphatic), 1688

(C=O), 1619 (C=C), 1596, 1482 and 1450 (aromatic), 1303 and 1144 (SO_2). ^{1}H NMR (300 MHz, $CDC1_3$): $\delta = 10.04$ (s, 1H), 7.99 (s, 1H), 7.92 (d, $J = 7.4$ Hz, 1H), 7.86 (d, $J = 8.2$ Hz, 2H), 7.74 (d, $J = 7.4$ Hz, 1H), 7.72 (d, $J = 15.4$ Hz, 1H), 7.60 (t, $J = 7.7$ Hz, 1H), 7.38 (d, $J = 8.2$ Hz, 2H), 6.99 (d, $J = 15.4$ Hz, 1H), 2.46 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 191.3$, 144.7, 140.0, 137.2, 136.9, 134.0, 133.5, 131.9, 130.1, 129.9, 129.7, 128.9, 127.8, 21.6. HRMS (ESI-TOF): m/z [M + Na$^+$] calcd. for $C_{16}H_{14}O_3SNa$: 309.0561; found: 309.0524.

(*E*)-1-Methyl-4-{[4-(tosylmethyl)styryl]sulfonyl}benzene (2l). White solid. Mp: 77–79 °C; $R_f = 0.20$ (hexanes–EtOAc, 7:3). IR (KBr): 3043 (aromatic), 2925 (aliphatic), 1610 (C=C), 1597, 1494 and 1446 (aromatic), 1303 and 1147 (SO_2) cm^{-1}. ^{1}H NMR (300 MHz, $CDC1_3$): $\delta = 7.79$ (d, $J = 8.2$ Hz, 2H), 7.57 (d, $J = 15.5$ Hz, 1H), 7.48 (d, $J = 8.2$ Hz, 2H), 7.35–7.31 (m, 4H), 7.21 (d, $J = 8.1$ Hz, 2H), 7.10 (d, $J = 8.1$ Hz, 2H), 6.85 (d, $J = 15.5$ Hz, 1H), 4.28 (s, 2H), 2.40 (s, 3H), 2.38 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 145.0$, 144.6, 140.8, 137.5, 134.8, 132.8, 131.5, 131.3, 130.0, 129.7, 128.56, 128.55, 127.8, 62.6, 21.64, 21.62. HRMS (ESI-TOF): m/z [M + Na$^+$] calcd. for $C_{23}H_{22}O_4S_2Na$: 427.1038; found: 427.1040.

(*E*)-1-[(Phenylsulfonyl)methyl]-4-[2-(phenylsulfonyl)vinyl]benzene (2ll). White solid. Mp: 160–162 °C; $R_f = 0.13$ (hexanes–EtOAc, 7:3). IR (KBr): 3050 (aromatic), 1615 (C=C), 1583, 1481 and 1447 (aromatic), 1299 and 1148 (SO_2). ^{1}H NMR (300 MHz, $CDC1_3$): $\delta = 7.97$ (d, $J = 7.3$ Hz, 2H), 7.67–7.56 (m, 7H), 7.48 (t, $J = 7.3$ Hz, 2H), 7.40 (d, $J = 8.1$ Hz, 2H), 7.14 (d, $J = 8.1$ Hz, 2H), 6.88 (d, $J = 15.4$ Hz, 1H), 4.34 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 141.3$, 140.4, 137.7, 134.0, 133.5, 132.8, 131.5, 131.2, 129.4, 129.1, 128.6, 128.5, 128.3, 127.7, 62.5. HRMS (ESI-TOF): m/z [M + Na$^+$] calcd. for $C_{21}H_{18}O_4S_2Na$: 421.0544; found: 421.0602.

General Procedure B

I_2 (380.7 mg, 1.5 mmol) was added to a suspension mixture of aliphatic alkene (or activated alkene) (0.5 mmol) and *p*-TolSO_2Na (356.4 mg, 2.0 mmol) in CH_3CN (2 mL), and the reaction mixture was vigorously stirred at refluxing temperature for 1 h. After cooling to room temperature, NaOAc (61.5 mg, 0.75 mmol) was added and the reaction mixture was vigorously stirred at refluxing temperature for 0.5 h. Upon completion of the reaction, the reaction mixture was quenched by the addition of saturated aqueous sodium thiosulfate ($Na_2S_2O_3$) (5 mL), and basified with saturated aqueous sodium hydrogen carbonate ($NaHCO_3$) (5 mL). Further stirring was followed by extraction with ethyl acetate (3 × 15 mL). The combined organic extracts were washed with water (20 mL) and brine (20 mL), dried (anhydrous $MgSO_4$), filtered, and concentrated (aspirator). The residue was purified by column chromatography (silica gel) to furnish the analytically pure product and all solids were recrystallized from hexanes/CH_2Cl_2.

(*E*)-1-Methyl-4-(oct-1-en-1-ylsulfonyl)benzene (4a). Colorless oil (lit.[4k] colorless viscous liquid); $R_f = 0.50$ (hexanes–EtOAc, 9:1). IR (neat): 3047 (aromatic), 2929 and 2858 (aliphatic), 1634 (C=C), 1597, 1495 and 1457 (aromatic), 1303 and 1146 (SO_2).^{1}H NMR (300 MHz, $CDC1_3$): $\delta = 7.75$ (d, $J = 8.3$ Hz, 2H), 7.32 (d,

$J = 8.0$ Hz, 2H), 6.95 (dt, $J = 15.1$, 6.9 Hz, 1H), 6.29 (d, $J = 15.1$ Hz, 1H), 2.42 (s, 3H), 2.21 (q, $J = 6.7$ Hz, 2H), 1.46–1.39 (m, 2H), 1.30–1.25 (m, 6H), 0.85 (br t, $J = 6.9$ Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 146.6$, 144.0, 137.7, 130.5, 129.72, 129.67, 127.4, 31.3, 28.5, 27.4, 22.3, 21.4, 13.8. HRMS (ESI-TOF): m/z [M + Na$^+$] calcd. for $C_{15}H_{22}O_2SNa$: 289.1238; found: 289.1188.

(*E*)-3-Tosylacrylamide (6e). White solid. Mp: 184–187 °C; $R_f = 0.18$ (hexanes–EtOAc, 4:1). IR (KBr): 3416 (N-H) 3070 (aromatic), 1678 (C=O), 1619 (C=C), 1601, 1490 and 1440 (aromatic), 1307 and 1150 (SO_2). ^{1}H NMR (300 MHz, acetone-d_6): $\delta = 7.81$ (d, $J = 8.3$ Hz, 2H), 7.60–7.40 (br, 1H), 7.48 (d, $J = 8.0$ Hz, 2H), 7.32 (d, $J = 14.9$ Hz, 1H), 7.01 (d, $J = 14.9$ Hz, 1H), 7.05–6.85 (br, 1H), 2.44 (s, 3H). ^{13}C NMR (75 MHz, acetone-d_6): $\delta = 164.1$, 146.1, 141.1, 137.6, 134.9, 131.0, 128.9, 21.5. HRMS (ESI-TOF): m/z [M + Na$^+$] calcd. for $C_{10}H_{11}NO_3SNa$: 248.0357; found: 248.0327.

(*E*)-2-Methyl-3-tosylacrylonitrile (6ga). White solid. Mp: 93–94 °C; $R_f = 0.25$ (hexanes–EtOAc, 8.5:1.5). IR (KBr): 3038 (aromatic), 2924 (aliphatic), 2233 (C≡N), 1594 and 1440 (aromatic), 1299 and 1149 (SO_2). ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.82$ (d, $J = 8.4$ Hz, 2H), 7.43 (d, $J = 8.0$ Hz, 2H), 6.89 (d, $J = 1.6$ Hz, 1H), 2.50 (s, 3H), 2.42 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 146.0$, 143.1, 136.8, 130.4, 127.9, 123.2, 117.1, 21.6, 16.4. HRMS (ESI-TOF): m/z [M + Na$^+$] calcd. for $C_{11}H_{11}NO_2SNa$: 244.0408; found: 244.0381.

(*Z*)-2-methyl-3-tosylacrylonitrile (6gb). White solid. Mp: 112–114 °C; $R_f = 0.10$ (hexanes–EtOAc, 8.5:1.5). IR (KBr): 3038 (aromatic), 2924 (aliphatic), 2233 (C≡N), 1619 (C=C), 1594 and 1441 (aromatic), 1307 and 1149 (SO_2). ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.88$ (d, $J = 8.4$ Hz, 2H), 7.41 (d, $J = 8.0$ Hz, 2H), 6.87 (q, $J = 1.6$ Hz, 1H), 2.47 (s, 3H), 2.16 (d, $J = 1.6$ Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 145.9$, 142.9, 135.9, 130.2, 128.2, 121.1, 114.2, 22.3, 21.6. HRMS (ESI-TOF): m/z [M + Na$^+$] calcd. for $C_{11}H_{11}NO_2SNa$: 244.0408; found: 244.0376.

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