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Communication

Ultrasound-Promoted Chemoselective Oxysulfonylation of Alkenes

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The ultrasound-assisted oxysulfonylation of different alkenes using sodium salts of organosulfinic acids under air atmosphere is described. The reaction is chemo- and regioselective and the corresponding β-keto-sulfones were obtained in good yields as major products. The use of ultrasound greatly accelerated the formation of products when compared to the conventional methods.

Keywords: ultrasound, oxysulfonylation, iron trichloride, β-keto-sulfones

Introduction

The synthesis of organosulfur compounds experienced a tremendous growth in the last years.[1] This is particularly true for β-keto-sulfones due to their applications in the synthesis of natural products[2] and heterocyclic compounds[3] as well as to their biological properties.[4] These qualities led to the emergence of several methods for the synthesis of these compounds and strategies based on the oxidation of β-keto-sulfides,[5] alkylation using α-halo-ketones,[6] acylation of methyl sulfones[7] and sulfonylation of methyl ketones[8] using a variety of substrates were described. However, most of them have some limitations such as being non-catalytic, involving multi-step synthesis of the starting materials, or the use of harsh conditions to promote the reaction.

The oxysulfonylation of alkenes or alkynes appeared as an easy alternative for the synthesis of β-keto-sulfones. The oxysulfonylation is based on the reaction of alkenes or alkynes with sulfonyl radicals. These radicals can be generated from readily available starting materials, being sulfonyl halides,[9] sulfonylhydrazides,[10,11] or the oxidation of sulfonates,[12] the most commonly used due to the high atomic efficiency.[13,14] Despite these characteristics, all these methods require long reaction times, heating and/or the use of a variety of additives to promote the reaction effectively. Accordingly, the development of a simpler method that could make the oxysulfonylation reaction more efficient in terms of yield and reaction time would be of the great interest.

Lei and co-workers[15] described the generation of sulfonyl radicals from sulfinic acids in the presence of pyridine and dioxygen for the synthesis of β-hydroxy-sulfones. It is also well-known that the activation of dioxygen mostly proceeded by a radical process.[16]

Within this context, the use of ultrasound as a source of hydroxyl radical and other reactive oxygen species through the formation, growth and implosive collapse of microbubbles in a liquid could result in an unusual reaction environment within and in the vicinity of bubbles.[17] These characteristics make the use of ultrasound irradiation a common partner in a variety of areas such as organic and organometallic chemistry, materials science, aerogels, food chemistry and medicinal research.[18,19]

In addition, the use of ultrasound is in accordance to the principles of sustainable chemistry, while the demand for methods based on the use of less hazardous chemicals and/or solvents, and the reduction of used energy is an expanding area.[20]

Experimental

General methods

All reagents and solvents used were previously purified and dried in agreement with the literature.[21] $FeCl_3$ (97%),

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alkenes **1a**-**g**, **1i**, **1j** and **1l** and sodium sulfinates, **2a**-**d**, were purchased from Aldrich Chemical Co. and used as received. Reactions were monitored by thin-layer chromatography (TLC) on 0.25 mm E. Merck silica gel 60 plates (F254) using UV light, vanillin and *p*-anisaldehyde as visualizing agents. ^{1}H and ^{13}C nuclear magnetic resonance (NMR) data were recorded in $CDCl_3$. The chemical shifts are reported as delta (δ) units in parts *per* million (ppm) relative to the solvent residual peak as the internal reference. ^{11}B NMR spectrum (128 MHz) was obtained in $CDCl_3$. Spectrum was calibrated using BF_3•Et_2O (0.0 ppm) as external reference.[22] Coupling constants (*J*) for all spectra are reported in hertz (Hz). The sonication was performed in an 8890E-DTH ultrasonic cleaner (with a frequency of 47 kHz and a nominal power 35 W; Cole Parmer Co.). The reaction flask was located at the maximum energy area in the cleaner, the surface of reactants was slightly lower than the level of the water. The reaction temperature was controlled by water bath.

General procedure for the synthesis of β-keto-sulfones (**3a**-**o**)

In a 25 mL round-bottomed flask containing $FeCl_3$ (0.05 mmol, 8.2 mg) in a 2:1 mixture of MeCN:H_2O (3 mL), it was added the appropriate sodium sulfinate (1.5 mmol), alkene (0.25 mmol) and $(NH_4)_2S_2O_8$ (0.05 mmol, 11.5 mg). The mixture was placed on an ultrasound bath and irradiated for 1 h.

After this period, the mixture was diluted with CH_2Cl_2 (5 mL) and washed with H_2O (3 × 15 mL). The organic phase was dried under anhydrous $MgSO_4$, filtered and the solvent removed *in vacuo*. The residue was purified by silica gel chromatographic column [hexanes:EtOAc (8:2)] to yield the corresponding products.

1-Phenyl-2-(phenylsulfonyl)ethanone (**3a**)

Obtained 53.4 mg (82%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* 8.2 Hz, 2H, H_{Aryl}), 7.89 (d, *J* 8.2 Hz, 2H, H_{Aryl}), 7.68-7.89 (m, 2H), 7.54 (t, *J* 7.4 Hz, 2H, H_{Aryl}), 7.47 (t, *J* 7.4 Hz, 2H, H_{Aryl}), 4.74 (s, 2H, –CH_2–); ^{13}C NMR (100 MHz, $CDCl_3$) δ 187.9, 138.7, 135.7, 134.3, 134.2, 129.25, 129.17, 128.8, 128.5, 63.4. The data match with the previously described compound.[23]

1-(Naphthalen-2-yl)-2-(phenylsulfonyl)ethanone (**3b**)

Obtained 48.9 mg (63%); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.48 (s, 1H, H_{Aryl}), 7.99-7.87 (m, 6H, H_{Aryl}), 7.68-7.52 (m, 5H, H_{Aryl}), 4.87 (s, 2H, –CH_2–); ^{13}C NMR (75 MHz, $CDCl_3$) δ 187.9, 138.7, 136.1, 134.3, 133.1, 132.3, 132.2, 130.0, 129.4, 129.2, 128.9, 128.6, 127.8, 127.2, 123.9, 63.7. The data match with the previously described compound.[23]

2-Phenyl-1-(phenylsulfonyl)propan-2-ol (**4c**)

Obtained 62.2 mg (90%); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.59 (d, *J* 7.0 Hz, 2H, H_{Aryl}), 7.52 (t, *J* 7.0 Hz, 1H, H_{Aryl}), 7.38 (t, *J* 7.6 Hz, 2H, H_{Aryl}), 7.30-7.27 (m, 2H, H_{Aryl}), 7.21-7.16 (m, 3H, H_{Aryl}), 4.61 (s, 1H, –O*H*), 3.75 (d, *J* 14.6 Hz, 1H, –CH_2–), 3.62 (d, *J* 14.6 Hz, 1H, –CH_2–), 1.71 (s, 3H, –CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 144.3, 140.2, 133.4, 129.0, 128.2, 127.4, 127.2, 124.6, 73.1, 66.6, 30.7. The data match with the previously described compound.[24]

1-(4-Fluorophenyl)-2-(phenylsulfonyl)ethanone (**3e**)

Obtained 46.6 mg (67%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02-7.98 (m, 4H, H_{Aryl}), 7.89 (d, *J* 7.6 Hz, 2H, H_{Aryl}), 7.69 (t, *J* 7.8 Hz, 2H, H_{Aryl}), 7.56 (t, *J* 7.8 Hz, 2H, H_{Aryl}), 7.17 (t, *J* 8.6 Hz, 2H, H_{Aryl}), 4.71 (s, 2H, –CH_2–); ^{13}C NMR (100 MHz, $CDCl_3$) δ 186.3, 166.5 (d, *J* 256.5 Hz), 165.2, 138.6, 134.2, 132.2, 129.2, 128.5, 116.2, 116.0, 63.6. The data match with the previously described compound.[23]

1-(4-Methoxyphenyl)-2-(phenylsulfonyl)ethanone (**3f**)

Obtained 37.7 mg (52%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94-7.88 (m, 4H, H_{Aryl}), 7.67 (t, *J* 7.2 Hz, 2H, H_{Aryl}), 7.55 (t, *J* 7.4 Hz, 2H, H_{Aryl}), 6.95 (d, *J* 8.2 Hz, 2H, H_{Aryl}), 4.69 (s, 2H, –CH_2–), 3.89 (s, 3H, OCH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 186.1, 164.5, 138.7, 134.1, 131.8, 129.1, 128.8, 128.5, 114.1, 63.5, 55.6. The data match with the previously described compound.[23]

1-(4-Methoxyphenyl)-2-(phenylsulfonyl)ethanol (**4f**)

Obtained 18.3 mg (25%); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.95 (d, *J* 7.6 Hz, 2H, H_{Aryl}), 7.71-7.68 (m, 1H, H_{Aryl}), 7.61-7.56 (m, 2H, H_{Aryl}), 7.20 (d, *J* 8.8 Hz, 2H, H_{Aryl}), 6.83 (d, *J* 8.8 Hz, 2H, H_{Aryl}), 5.24-5.20 (m, 1H, –C*H*(OH)–), 3.77 (s, 3H, –OCH_3), 3.60 (d, *J* 8.8 Hz, 1H, OH), 3.51 (dd, *J* 14.7, 10.0 Hz, 1 H, –CH_2–), 3.32 (dd, *J* 14.7, 1.8 Hz, 1H, –CH_2–); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.5, 139.2, 134.0, 132.8, 129.4, 127.9, 126.9, 114.1, 68.0, 63.9, 55.3. The data match with the previously described compound.[24]

1-(4-Aminophenyl)-2-(phenylsulfonyl)ethanol (**4g**)

Obtained 62 mg (89%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, 2H, *J* 7.8 Hz), 7.68 (t, 1H, *J* 7.4 Hz), 7.58 (d, 2H, *J* 7.4 Hz), 7.06 (d, 2H, *J* 8.2 Hz), 6.61 (d, 2H, *J* 8.2 Hz), 5.15 (m, 1H), 3.51 (dd, 1H, *J* 9.8 and 4.3 Hz), 3.31 (dd, 1H, *J* 14 and 2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.6, 139.3, 133.9, 130.5, 129.3, 127.9, 126.9, 115.1, 68.2, 63.8.

1-Phenyl-2-(*p*-tolylsulfonyl)ethanone (**3m**)

Obtained 48.0 mg (70%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* 7.8 Hz, 2H, H_{Aryl}), 7.77 (d, *J* 8.3 Hz, 2H, H_{Aryl}), 7.63 (t, *J* 7.8 Hz, 1H, H_{Aryl}), 7.49 (t, *J* 7.8 Hz, 2H, H_{Aryl}),

7.34 (d, *J* 8.3 Hz, 2H, H_{Aryl}), 4.72 (s, 2H, –CH_2–), 2.45 (s, 3H, –CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.1, 145.3, 135.8, 134.3, 129.8, 129.3, 128.8, 128.6, 63.8, 21.7. The data match with the previously described compound.[23]

1-Phenyl-2-(methylsulfonyl)ethanone (**3n**)

Obtained 19.8 mg (40%); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.01 (d, *J* 7.6 Hz, 2H, H_{Aryl}), 7.67 (t, *J* 7.6 Hz, 1H, H_{Aryl}), 7.53 (t, *J* 7.0 Hz, 2H, H_{Aryl}), 4.61 (s, 2H, –CH_2–), 3.16 (s, 3H, –CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 189.2, 135.6, 134.7, 129.2, 129.0, 61.2, 41.8. The data match with the previously described compound.[23]

Results and Discussion

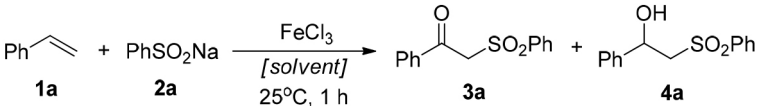
This work describes the use of ultrasound irradiation for the chemo- and regioselective synthesis of β-keto-sulfones based on the type reaction of alkenes and sodium salts of organosulfinic acids. In the course of developing milder reaction conditions, the effect of the solvent to promote the reaction was first examined. Thus, styrene, **1a** (0.25 mmol), and benzenesulfinic acid sodium salt, **2a** (0.375 mmol), were used as model compounds and treated at room temperature with $FeCl_3$ (20 mol%) using different solvents. The progress of the reaction was monitored by TLC and the results are depicted in Table 1.

From Table 1, it can be observed that mixtures of the corresponding β-keto-sulfone (**3a**) and β-hydroxy-sulfone (**4a**) were obtained in all cases with ratios depending on the type of solvent. When dichloromethane was used, a good conversion from **1a** to the products and a lower selectivity to the desired compound **3a** were observed (Table 1, entry 1). When water or tetrahydrofuran (THF) were used, lower conversions were also observed in both cases, probably due to the low solubility of starting materials in these solvents (Table 1, entries 2 and 3). Better results were observed when acetone or acetonitrile were used after 24 h of reaction (Table 1, entries 4 and 5). A dramatic effect occurred when the reaction was performed under sonication (Table 1, entries 6 to 8). When acetone or acetonitrile were used as the reaction solvent, an increment in both conversion and selectivity was observed, however, when a 2:1 mixture of acetonitrile and water was used, **3a** was obtained in better conversions and selectivities (Table 1, entry 8). The most evident effect of the use of ultrasound in the reaction was the reduction of the time from 24 h to only 1 h.

Next, the minimal amount of $FeCl_3$ necessary to promote the reaction under sonication was screened. The results are described on Table 2. Smaller amounts of catalyst favored the formation of β-hydroxy-sulfone (**4a**, Table 2, entries 1-3), however, an improvement in both conversion and selectivity was observed when the amount of $FeCl_3$ was increased to 20 and 30 mol% with no significant changes in the product ratio (Table 2, entries 4 and 5). Nonetheless, the increment in the amount of $FeCl_3$ to 40 mol% led to a decrease in both conversion and selectivity due to the formation of several by-products in the reaction (Table 2, entry 6). Therefore, the control of the amount of $FeCl_3$ used in the reaction is fundamental because it is directly related to the conversion and selectivity of the formed products.

As mentioned before, ultrasound irradiation can be used as a source of hydroxyl radical and other reactive oxygen species.[16] The combination of ultrasound irradiation and persulfate has been proved to be effective for removing several kinds of pollutants through the generation of both HO$^\bullet$ and $SO_4^{\bullet-}$.[25] Thus, it would be expected that by using

Table 1. $FeCl_3$ promoted oxysulfonylation of styrene **1a** using benzenesulfinic acid sodium salt, **2a**, in different solvents[a]

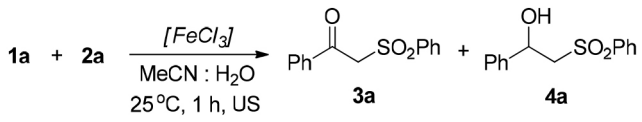


1a **2a** **3a** **4a**

entry	Solvent	time / h	**3a**[b] / %	**4a**[b] / %
1	CH_2Cl_2	24	39	30
2	H_2O	24	20	6
3	THF	24	5	–
4	acetone	24	67	18
5	MeCN	24	53	27
6[c]	acetone	1	61	20
7[c]	MeCN	1	75	4
8[c]	MeCN:H_2O[d]	1	82	6

[a]Reaction conditions: reactions were performed using **1a** (0.25 mmol), **2a** (0.375 mmol) and $FeCl_3$ (20 mol%) in the appropriate solvent (3 mL) at 25 °C; [b]determined by gas chromatography (GC) analysis; [c]the reaction was performed under sonication; [d]a 2:1 mixture was used.

Table 2. Oxysulfonylation of styrene, **1a**, using benzenesulfinic acid sodium salt, **2a**, using different amounts of $FeCl_3$[a]



entry	$FeCl_3$ / mol%	**3a**[b] / %	**4a**[b] / %
1	–	–	–
2	5	19	50
3	10	34	59
4	20	75	4
5	30	70	24
6	40	52	35

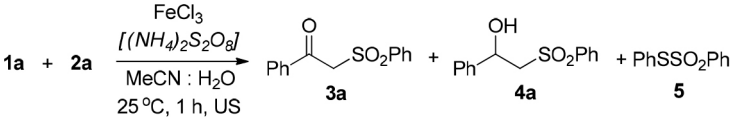
[a]Reaction conditions: reactions were performed using **1a** (0.25 mmol), **2a** (0.375 mmol) in MeCN:H_2O (3 mL) at 25 °C under sonication using the appropriate amount of $FeCl_3$; [b]determined by gas chromatography (GC) analysis.

the combination of ultrasound irradiation and persulfate, an increment not only in the formation of radicals would be observed, but also in the selectivity favoring the formation of **3a**. The use of a persulfate to accelerate the oxysulfonylation reaction through the formation of the sulfinyl radical was also recently described.[26-33] The results are described in Table 3.

Initially, the efficacy of the reaction was investigated using 20 mol% of ammonium persulfate [$(NH_4)_2S_2O_8$] as the oxidant, without $FeCl_3$. After 1 h, the reaction was not complete with much of the remaining starting material being observed together with a conversion of 39% to product **3a** and only traces of **4a** (Table 3, entry 2). The best result was observed when 20 mol% of $(NH_4)_2S_2O_8$ and 20 mol% of $FeCl_3$ were used, where excellent conversions and selectivities to the β-keto-sulfone **3a** were observed after 1 h (Table 3, entry 3). Additional increment in the amount of oxidant to 40 mol% resulted in 84% conversion to **3a** (Table 3, entry 4). Noteworthy, the corresponding thiosulfonate (**5**) was obtained as a byproduct in the reaction in a small amount. This result was later confirmed by increasing the amount of $(NH_4)_2S_2O_8$ and $FeCl_3$ to 100 mol%, where **4a** was obtained as the major product in the reaction together with the corresponding thiosulfonate **5** (Table 3, entry 5). Finally, a reaction under stirring using the optimized conditions was performed in order to compare the efficacy of ultrasound in the oxysulfonylation of styrene, **1a**. Using these conditions **3a** was obtained as the major product after 24 h reaction (Table 3, entry 6).

The optimized reaction conditions namely: **1a** (0.25 mmol), **2a** (0.375 mmol), $FeCl_3$ (20 mol%) and $(NH_4)_2S_2O_8$ (20 mol%) in MeCN:H_2O [3 mL (2:1)] under sonication for 1 h were then applied to different substrates in order to explore the scope of the method, as well as the electronic effects of the substituents on the reaction yields. The results are described on Table 4, where it can be seen that the method was efficient for most of the substrates used.

Table 3. Oxysulfonylation of styrene, **1a**, using benzenesulfinic acid sodium salt, **2a**, using different amounts of $FeCl_3$ and $(NH_4)_2S_2O_8$[a]



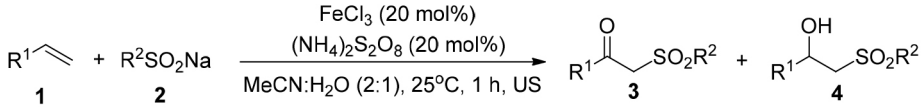
entry	$FeCl_3$ / mol%	$(NH_4)_2S_2O_8$ / mol%	**3a**[b] / %	**4a**[b] / %	**5**[b] / %
1	20	–	75	9	–
2	–	20	39	2	–
3	20	20	91	4	–
4	20	40	84	3	9
5	100	100	6	51	22
6[c]	20	20	80	10	–

[a]Reaction conditions: reactions were performed using **1a** (0.25 mmol), **2a** (0.375 mmol) and the appropriate amount of $FeCl_3$ and $(NH_4)_2S_2O_8$ in MeCN:H_2O (3 mL) at 25 °C under sonication for 1 h; [b]determined by gas chromatography (GC) analysis; [c]the reaction was performed under stirring for 24 h.

When compounds **1a** and **1b** were used as substrates together with the sulfinate **2a**, the desired products were obtained in good yields, being observed better selectivities when **1a** was used as substrate (Table 4, entries 1 and 2). When **1c** was used, the corresponding β-hydroxysulfone **4c** was obtained in 90% yield as the exclusive reaction product (Table 4, entry 3). The use of *trans*-stilbene (**1d**), a 1,2-disubstituted alkene, led to a complex mixture of products, and the isolation of **3d** and **4d** was not possible in this case (Table 4, entry 4).

The presence of deactivating groups such as the fluorine atom on the aromatic ring led preferentially to the β-keto-

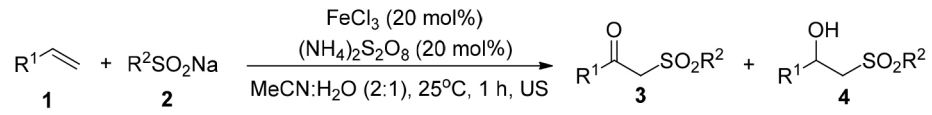
Table 4. Oxysulfonylation of different alkenes promoted by ultrasound

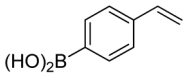
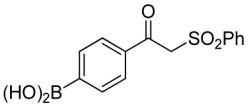
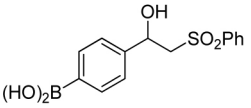
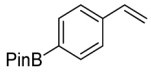
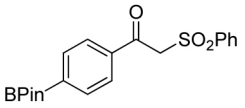
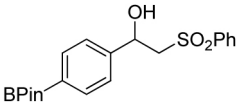
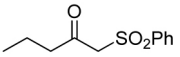
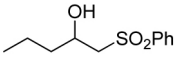
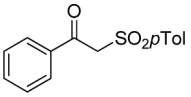
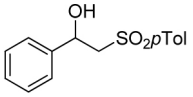
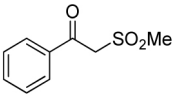
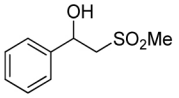
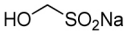
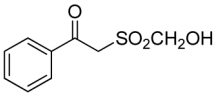
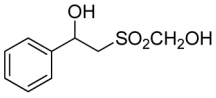


1 **2** **3** **4**

entry	1	2	3	4	3[a] / %	3:4[b]
1	**1a**	$PhSO_2Na$ **2a**	**3a**	**4a**	82	96:4
2	**1b**	**2a**	**3b**	**4b**	63[c]	71:29
3	**1c**	**2a**	**4c**		90	0:100
4	**1d**	**2a**	**3d**	**4d**	–[d]	–
5	**1e**	**2a**	**3e**	**4e**	67	95:5
6	**1f**	**2a**	**3f**	**4f**	52	67:33
7	**1g**	**2a**	**3g**	**4g**	89[e]	10:90
8	**1h**	**2a**	**3h**	**4h**	–[d]	–
9	**1i**	**2a**	**3i**	**4i**	–[f]	–

Table 4. Oxysulfonylation of different alkenes promoted by ultrasound (cont.)



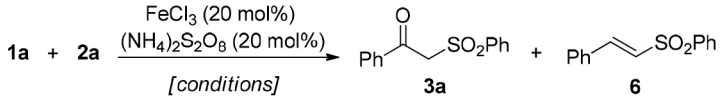
entry	1	2	3	4	3[a] / %	3:4[b]
10	 **1j**	**2a**	 **3j**	 **4j**	–	–
11	 **1k**	**2a**	 **3k**	 **4k**	–[g]	–
12	 **1l**	$PhSO_2Na$ **2a**	 **3l**	 **4l**	–	–
13	**1a**	*p*-$TolSO_2Na$ **2b**	 **3m**	 **4m**	70	90:10
14	**1a**	$MeSO_2Na$ **2c**	 **3n**	 **4n**	40	96:4
15	**1a**	 **2d**	 **3o**	 **4o**	–	–

[a]Isolated yield; [b]determined by gas chromatography (GC) analysis; [c]the reaction was sonicated for 2 h; [d]a complex mixture of products was obtained; [e]the yield refers to the mixture of compounds **3g** and **4g**; [f]the corresponding phosphinoxide was obtained as product; [g]the corresponding boronic acid **1j** was obtained as product.

sulfone (**3e**) in moderate yield (Table 4, entry 5). Moreover, when 4-methoxyvinylbenzene (**1f**) was used as substrate, a decrease in yield and in the selectivity of the reaction was observed, where the desired product **3f** was obtained in 52% yield in a ratio of 67:33 (Table 4, entry 6). These results indicate that the electronic effects can influence both the yield and the selectivity of the reaction and that the presence of donor groups in the starting alkene would favor the formation of β-hydroxysulfone. This observation was confirmed when 4-vinylaniline (**1g**) was subjected to the same reaction conditions, where the corresponding products **3g** and **4g** were obtained in 89% yield as an inseparable mixture, being the β-hydroxysulfone (**4g**) the major product (Table 4, entry 7). When amide **1h** was used as substrate, a complex mixture of products was obtained (Table 4, entry 8). When 4-(diphenylphosphino)-styrene (**1i**) was used in the reaction, the expected products **3i** and **4i** were not observed, and the only product obtained in the reaction was the corresponding phosphinoxide (Table 4, entry 9). This fact indicated that the presence of some functionalities containing a Lewis base character in the starting material would be troublesome when performing the reaction.

A study of the behavior of the reaction in the presence of Lewis acids, such as boronic acid **1j**, was also performed. In this case, a complex mixture of products was observed in the reaction (Table 4, entry 10). When the corresponding boronic ester **1k** was used in the oxysulfonylation reaction, the only product observed was the boronic acid **1j**, probably due to the presence of water and $FeCl_3$ in the reaction medium (Table 4, entry 11). This result is in agreement with the literature,[34] where it is described that the hydrolysis of some boron compounds can occur in the presence of $FeCl_3$. Finally, when 1-pentene (**1l**) was used as the substrate, the desired product **3l** was not observed (Table 4, entry 12).

Table 5. Oxysulfonylation of styrene, **1a**, using benzenesulfinic acid sodium salt, **2a**, under argon atmosphere[a]



entry	Condition	**3a**[b] /%	**6**[b] /%
1	MeCN, 25 °C, 1 h,))), Ar	19	14
2	MeCN, TEMPO, 25 °C, 1 h,))), Ar	–	–

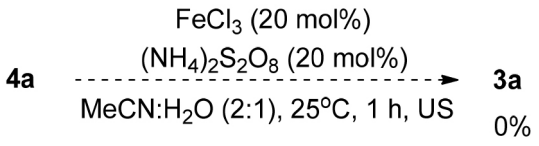
[a]Reaction conditions: reactions were performed using **1a** (0.25 mmol), **2a** (0.375 mmol) in MeCN (3 mL) under argon; [b]determined by gas chromatography (GC) analysis. TEMPO: (2,2,6,6-tetramethylpiperidin-1-yl)oxyl.

The use of different sodium sulfinates in the oxysulfonylation of alkenes promoted by ultrasound was also evaluated. When styrene **1a** and sodium sulfinate **2b** were used, similar yields and selectivities were observed (Table 4, entries 1 and 13). However, when sodium methanesulfinate **2d** was used, the corresponding product **3n** was obtained in only 40% yield with a high selectivity, favoring the β-keto-sulfone (Table 4, entry 14). Finally, when sodium hydroxymethanesulfinate **2c** was used, the corresponding products were not observed (Table 4, entry 15).

In an attempt to obtain some information about the mechanism of the reaction, some additional experiments were performed. First, the optimized conditions were applied for the reaction of **1a** and **2a** under argon atmosphere using only anhydrous acetonitrile as solvent (Table 5, entry 1). In this case, **3a** was obtained in a low conversion together with the corresponding vinyl sulfone, **6**.

Next, the reaction was performed in presence of (2,2,6,6-tetramethylpiperidin-1-yl)oxyl (TEMPO), a radical scavenger (Table 5, entry 2). In this specific case, the desired product **3a** was not observed and only the starting materials were recovered. The results described in Table 5 indicated that the presence of oxygen is important for the oxysulfonylation reaction and are in agreement with those previously described in the literature.[16]

Noteworthy, when the reaction was carried out using the β-hydroxysulfone **4a** as the substrate under the optimized reaction conditions, the corresponding β-keto-sulfone **3a** was not observed indicating that **4a** was not the intermediate in the reaction (Scheme 1).

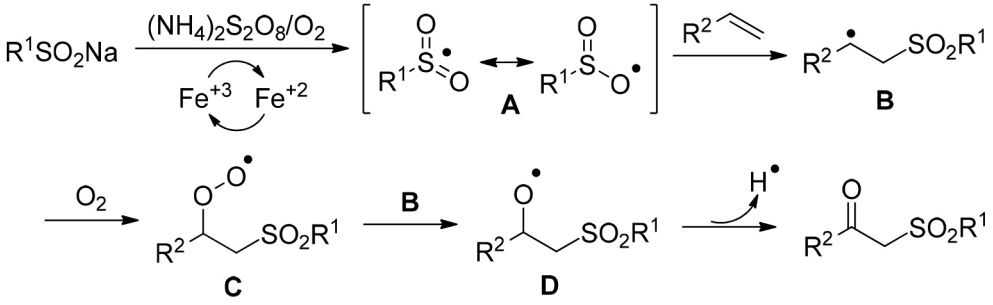


Scheme 1. Attempt to synthesize **3a** from **4a**.

The suggested reaction mechanism was proposed by Huang and co-workers[35] and Yadav and co-workers,[36] which is based on the generation of an oxygen-centered radical and its resonance structure sulfonyl radical A (Scheme 2). The capture of this radical by the appropriate alkene would lead to a carbon-centered radical B, which would be trapped by O_2 to give the corresponding peroxyl radical C. Further reaction with radical B to generate the oxyl radical D followed by hydrogen radical abstraction would give the β-keto sulfone (Scheme 2).

Conclusions

In summary, we have demonstrated the ultrasound-assisted oxysulfonylation of different alkenes using sodium salts of organosulfinic acids under air atmosphere in a very chemo- and regioselective way. The corresponding β-keto-sulfones were obtained in short reaction time when



Scheme 2. Suggested mechanistic pathway.

compared to other procedures described in the literature, high yield and purity. The method is simple, fast and general, allowing further applications in the synthesis of more complex compounds.

Supplementary Information

Additional experimental procedures and spectroscopic characterization data, as well as ^{1}H, ^{13}C and ^{11}B NMR spectra for all synthesized compounds are available free of charge at http://jbcs.sbq.org.br as PDF file.

Acknowledgments

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