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Graphical Abstract

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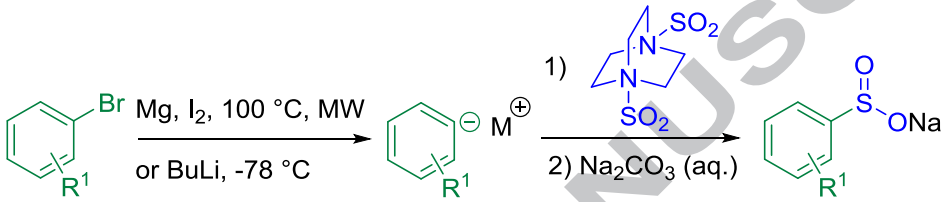

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Synthesis of sodium aryl sulfinates from aryl bromides employing 1,4-diazabicyclo[2.2.2]octane bis(sulfur dioxide) adduct (DABSO) as a bench-stable, gas-free alternative to SO_2

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ABSTRACT

A convenient two-step protocol for the synthesis of sodium aryl sulfinates from aryl bromides and the SO_2 surrogate 1,4-diazabicyclo[2.2.2]octane bis(sulfur dioxide) adduct (DABSO) has been developed. A wide range of aryl bromides with respect to electronic properties were employed to give the corresponding sodium arylsulfinates in good to excellent yields. The protocol is especially efficient for electron poor aryl bromides which are often difficult to prepare using existing methods.

Introduction

Until recently, sulfinic acids and their corresponding salts have received relatively little attention in the literature. The properties and reactivity of sulfinates were first reported in the beginning of the 1900s[1–3] and sulfinic acids exist in biological systems *e*.g. cysteine is naturally reversibly oxidized to cysteine sulfinic acid.[4] However, sulfinates are highly valuable precursors in organic synthesis and have re-emerged as potential coupling partners in the last decade.[5] Sulfinates can act as either electrophilic or nucleophilic agents depending on the reaction conditions, resulting in either a sulfonylative or desulfitative process. Sulfinates react with dinitrogen tetraoxide to form sulfonyl nitrites[6] or to form sulfonyl thioesters in the presence of thiols.[7] Sulfinates can also form sulfonyl cyanides by the reaction with cyanogen chloride[8] or can react directly with sulfur to form sodium methanethiosulfonate.[9] Sulfinic acids may be reduced to disulfides,[10,11] which has been found to be a key process in the sulfenylation of indoles by sulfinic acids in the presence of toluenesulfonic acid and *n*-Bu_4NI.[12] Sodium sulfinates treated with trifluoromethanesulfonic acid act as electrophiles in electrophilic aromatic substitution reactions to give the corresponding aryl sulfoxides.[13] Gem-difluoroolefination of aldehydes and ketones has been effected by a desulfitative process using *in situ* generated sodium sulfinates.[14] Sulfinates also constitute sulfonyl radical precursors and can react with iodine to form sulfonyl iodides that can be homolytically cleaved to form sulfonyl radicals[15] or can alternatively undergo direct oxidation by TBHP[16] or CAN.[17] Sulfinates can also undergo metal-free decarboxylative couplings with cinnamic acids in DMSO by a radical mechanism to form vinyl sulfones.[18] Sulfinic acids react *via* a postulated radical mechanism with NBS to form sulfonyl bromides, which were exploited in the synthesis of β-bromo sulfones from sulfinic acids and styrenes.[19]

Sodium aryl sulfinates have become a valuable alternative to boronic acids in Pd(II) catalyzed reactions and can be used as aryl palladium precursors in a wide range of reactions. Sonogashira[20] and Heck type[21–24] de-sulfurisation reactions have been developed in addition to protocols for conjugate 1,4-addition.[25,26] Sodium aryl sulfinates can also be used in Pd catalyzed phosphonation reactions[27] and a growing number of C-H arylation reactions of heteroarenes such as azoles,[28,29] indoles,[30,31] coumarins[24] and polyfluoroarenes[32] exploiting sodium sulfinates have been reported.

Sodium sulfinates are commonly prepared by reduction of the corresponding sulfonyl chlorides in an aqueous mixture of sodium sulfite and sodium bicarbonate.[33] Other strategies for the preparation of sulfinates include the reaction between sulfonyl chlorides and zinc to generate bis(alkanesulfinates),[34,35] Pd catalyzed coupling of diazonium tetrafluoroborates with SO_2 and H_2[36] or Friedel-Crafts sulfination with sulfonyl chlorides.[37]

The most straightforward retrosynthetic approach to sulfinates is the reaction between an organometallic reagent and sulfur dioxide (SO_2). Examples of the synthesis of sulfinic acids from Grignard[38,39] and organolithium reagents[40] exist in the literature, however the use of toxic and corrosive SO_2 gas is cumbersome as

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it requires careful handling and specialized equipment. This fact has prompted the development of solid SO_2 surrogates for *in situ* generation of the desired reactant.[41] Indeed, Willis and co-workers,[42–44] Rocke and co-workers[45] and Kopka and co-workers[46] have demonstrated that Grignard reagents and organolithium reagents or organozinc reagents, respectively, can be employed with the sulfur dioxide surrogate 1,4-diazabicyclo[2.2.2]octane bis(sulfur dioxide) adduct (DABSO) to generate sulfinates *in situ* for subsequent reaction. Recently, the use of DABSO for the synthesis of aryl sulfones *via* an aryl sulfinic acid intermediate was reported[47] and reaction with amines under treatment with sodium hypochlorite afforded the corresponding sulfonamides. Arylsulfonyl alkynes have been synthesized in a similar fashion through the reaction of Grignard reagents with DABSO and then subsequently with ethynyl-benziodoxolone (EBX) reagents.[48] Interestingly, the same results could be achieved using a palladium catalyst, and has been exploited in the synthesis of sulfones and sulfonamides *via* aryl sulfinates from the corresponding boronic acids.[49]

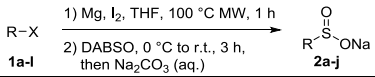
Inspired by the one-pot protocols mentioned above and based on our previous work with Pd(II) catalyzed addition of sodium sulfinates to nitriles,[50,51] we attempted to develop a one-pot, two step synthesis of aryl ketones from aryl bromides, DABSO and nitriles. However, the reactions only resulted in trace amounts of the desired product and excessive disproportionation of the sulfinate. Sulfinic acids are generally prone to oxidation in air and disproportionation *via* the corresponding sulfinyl sulfone occurs readily even in the absence of air and moisture.[52] Consequently, methods for the isolation of sulfinic acids are scarce and isolation as their corresponding salts is advantageous. Although valuable and elegant methods for *in situ* generation of sulfinates from DABSO and organometallic reagents in one-pot syntheses exist, to the best of our knowledge, no protocols for the synthesis and isolation of sodium sulfinates have been reported. Therefore we have focused our efforts on developing a convenient method for synthesizing and isolating sodium arylsulfinates. Herein, we report the gas-free synthesis of sodium sulfinates from Grignard and organolithium regents using the SO_2 surrogate DABSO.

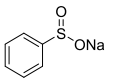
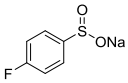
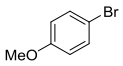
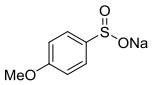
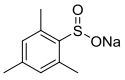
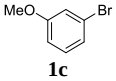
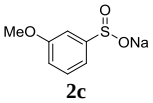
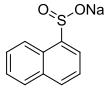
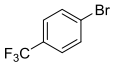
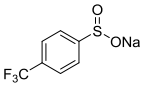
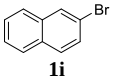
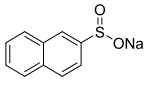
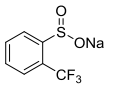
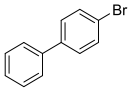
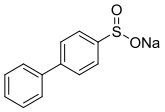
Results and discussion

As a starting point for our investigation, a model reaction between commercially available phenyl magnesium chloride and DABSO in THF was conducted. This resulted in almost quantitative conversion to the corresponding sulfinate **2a**, however purification of the crude sulfinic acid by extraction using 2 M HCl afforded only a mixture of the sulfinate and the corresponding sulfonic acid. Indeed, the HCl mediated disproportionation of sulfinic acids to sulfonic acid has been previously reported[53] leading us to examine a purification protocol employing sulfuric acid.[36] Unfortunately, purification of the sulfinic acid by silica gel, aluminum oxide or reverse phase chromatography resulted in almost quantitative conversion to the corresponding sulfonic acid. In order to avoid this unwanted oxidation, we focused our attention on the isolation of the sulfinate salt by treatment with aqueous Na_2CO_3 and purification by liquid-liquid and solid-liquid extraction. Rewardingly, this strategy afforded **2a** in 90% yield without any traces of phenyl sulfonic acid.

In order to develop a useful protocol for the synthesis of sodium arylsulfinates, the reaction conditions were optimized for the generation of phenyl magnesium bromide and subsequent reaction with DABSO. Although the halogen-metal exchange reagent *i*PrMgCl*LiCl can be used for this process,[54] it often requires long reaction times especially when using neutral or electron-rich aryl bromides as substrates. As we were interested in developing a rapid process, we employed a microwave heated protocol for generation of the Grignard reagents.[55] A number of solvents were therefore screened (diethyl ether, THF and *tert*-butyl methyl ether) and THF was identified as the solvent of choice. Thus, preparation of the Grignard reaction from bromobenzene, Mg and I_2 in THF under microwave irradiation at 100 °C for 1 h afforded **2a** in a good yield of 72%. The microwave-assisted protocol was found to be the most efficient for aryl bromides as chlorobenzene and iodobenzene furnished **2a** in yields of 64% and 25%, respectively (Table 1, entry 1). The low yield in the reaction with iodobenzene is due to the competing biaryl formation *via* a Wurtz-Fittig type reaction.[56] Based on these results, we continued our investigation with a focus on the use of aryl bromides.

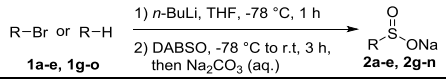
Table 1. Preparation of sulfinic acids by the reaction of Grignard reagents with DABSO.

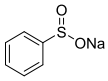
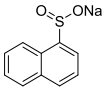
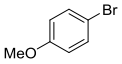
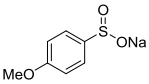
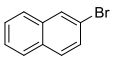
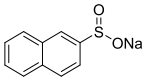
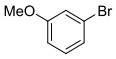
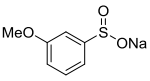
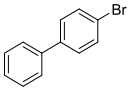
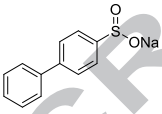
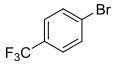
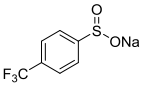
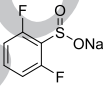
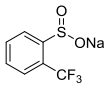
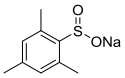
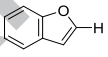
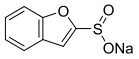


Entry	Aryl bromide	Product	Yield[a]	Entry	Aryl bromide	Product	Yield[a]
1	 **1a**	 **2a**	Cl: 64% /90%[b] Br: 72% I: 25%	6	 **1f**	 **2f**	74%
2	 **1b**	 **2b**	48%	7	 **1g**	 **2g**	69%
3	 **1c**	 **2c**	85%	8	 **1h**	 **2h**	48%
4	 **1d**	 **2d**	91%	9	 **1i**	 **2i**	47%
5	 **1e**	 **2e**	75%	10	 **1j**	 **2j**	87%

[a]Isolated yield, > 95% purity.
[b]Commercial phenyl magnesium chloride was used.

Table 2. Preparation of sodium sulfinates by the reaction of aryl lithium reagents with DABSO.



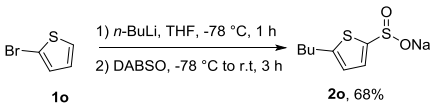
Entry	Aryl bromide	Product	Yield[a]	Entry	Aryl bromide	Product	Yield[a]
1	 **1a**	 **2a**	85%	7	 **1h**	 **2h**	82%
2	 **1b**	 **2b**	59%	8	 **1i**	 **2i**	73%
3	 **1c**	 **2c**	91%	9	 **1j**	 **2j**	42%
4	 **1d**	 **2d**	48%	10	 **1k**	 **2k**	62%
5	 **1e**	 **2e**	99%	11	 **1l/1m**	 **2l/2m**	X = S: 15%[b] X = O: 21%[b]
6	 **1g**	 **2g**	64%	12	 **1n**	 **2n**	50%[b]

[a]Isolated yield, > 95% purity.
[b]Reaction performed using *t*-BuLi.

To explore the scope and limitations of this reaction, a number of aryl bromides were screened. In general, electron-poor substrates were found to be more productive substrates as can be seen by comparison of the reactions with 4-methoxy and 3-methoxy-bromobenzene (Table 1, entries 2 and 3). Similarly, the electron poor 4-CF_3-bromobenzene gave an excellent yield of the desired product (Table 1, entry 4). Moving the substituent to the *ortho* position resulted in a lower yield (Table 1, entry 5) most probably due to unfavorable steric effects. Interestingly, the highly sterically congested 2,4,6-trimethyl-bromobenzene returned the corresponding sulfinate in 69% yield (Table 1, entry 6). 4-Bromobiphenyl was also found to be a productive substrate and returned a very good yield of **2j** (Table 1, entry 10), which is inaccessible through the common protocol employing sulfonyl chlorides in an aqueous solution due to poor solubility of the starting material in water.

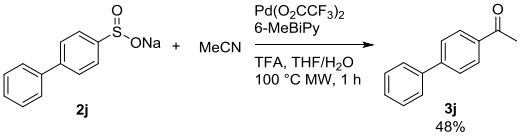
To further expand the utility of the developed reaction, the two-step synthesis of sodium arylsulfinates by lithiation of aryl bromides was also investigated (Table 2). The yields for the synthesis of sodium aryl sulfinates *via* the lithium reagents were generally similar to the corresponding Grignard reactions. The synthesis of **2a** *via* lithiation and reaction with DABSO afforded the desired product in very good yield (Table 2, entry 1). The same trend toward favoring electron poor substrates was also observed and 3-methoxy substituted bromobenzene afforded higher yield than the 4-methoxy substituted regioisomer (91% compared to 59%; entries 3 and 2, respectively). Interestingly, the use of 4-CF_3-bromobenzene resulted in significantly lower yield than using 2-CF_3-bromobenzene – contrary to the trend seen for the Grignard reagents (compare Table 2, entries 4 and 5 to Table 1, entries 4 and 5). The low yield of sodium 4-biphenyl sulfinate (Table 2, entry 9) can be explained by the poor solubility of the aryl lithium reagent and problematic addition to the reaction mixture.

Attempted lithium-halogen exchange of 2-bromo-thiophene at -78 °C resulted in lithium halogen exchange and nucleophilic attack by 2-lithiothiophene on butyl bromide, followed by subsequent reaction with DABSO to give butyl-thiophene sulfonate **2o** in 68% yield (Scheme 1).



Scheme 1. Attempted preparation of sodium thiophene sulfinate by generation of lithium reagent by *n*-BuLi and subsequent reaction with DABSO.

Lithiation of thiophene with *n*-BuLi at -78 °C was sluggish and a mixture of thiophene sulfinate and butyl sulfinate was obtained. Using more reactive *t*-BuLi gave the desired thiophene sulfinate albeit in low yield due to the high polarity of the product (Table 2, entry 11). However, when the more hydrophobic benzofuran was employed in the reaction the desired sulfinate was isolated in an improved yield of 50% (Table 2 entry 12).



Scheme 2. Pd(II) catalyzed addition of sodium aryl sulfinate **2j** to acetonitrile.

Finally, the novel sodium sulfinate **2j** was applied in a Pd(II) catalyzed addition to acetonitrile to afford the acetyl derivative **3j** in 48% yield, (Scheme 2). 4-Acetyl biphenyls such as the product **3j** are compounds that have diverse uses such as in the synthesis

of pyrazolines and isoxazolines with anti-malarial activity[57] and as sensitizers in thermal recording materials.[58]

Conclusion

The reaction between aryl Grignard or aryl lithium reagents and DABSO is a convenient and safe route to a wide range of sodium arylsulfinates. Although both electron poor and electron rich aryl bromides can be used, higher yields were obtained with electron poor substrates. Sixteen examples of sodium arylsulfinates were prepared including four heteroaryl sulfinates, and sodium 4-biphenyl sulfinate which is not accessible through reduction of the corresponding sulfonyl chlorides. Furthermore, the use of this sodium sulfinate in Pd(II) catalyzed addition to acetonitrile was demonstrated. The route *via* aryl lithium reagents generally gives higher yields of the desired product, although for the synthesis of sodium 4-biphenyl sulfinate the route *via* the corresponding Grignard reagent is preferred due to better solubility.

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Supplementary data

Supplementary data (experimental details, LCMS, GCMS, ^{1}H NMR, ^{13}C NMR, ^{19}F NMR and HRMS spectra) associated with this article can be found, in the online version, at DOI:

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