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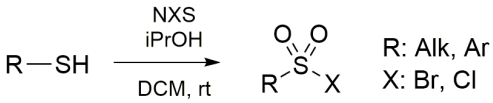

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Sulfonyl halide synthesis by thiol oxyhalogenation using NBS/NCS - *i*PrOH

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ABSTRACT

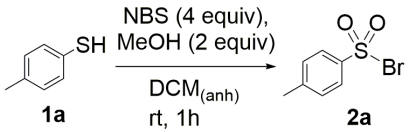
A rapid and facile method provides a general route to sulfonyl bromides/chlorides by the oxidation of thiols using NXS – ROH (X=Br,Cl, R=*i*Pr) as an oxyhalogenation reagent. Control experiments suggest that the alcohol component is the source of oxygen. The proposed method enable the access to structurally diverse sulfonyl bromides and chlorides including challenging sulfonyl halides, inaccessible by other synthetic methods.

Applications of sulfonyl halides are ubiquitous in synthetic organic chemistry. Sulfonyl chlorides are the most prevalent reagents for the installation of the sulfonyl protecting group,[1,2] or as activators of selected functional groups.[2] Sulfonyl chlorides and bromides have been extensively employed as precursors of sulfonyl derivatives, such as sulfonamides[3] and sulfonates.[2,3f,4] Interestingly, while bromide building blocks and reactants are considered synthetically more valuable than the chloride analogs,[5] sulfonyl bromides have not been exploited with the same frequency as the sulfonyl chloride counterparts.[6]

A literature survey evidences the oxyhalogenation of less-oxidized sulfur precursors as the main approach for the preparation of the sulfonyl chlorides and bromides. In most cases, the oxyhalogenation is performed in an aqueous reaction environment[3a,3d,3h,7] that serves as an oxygen source for installment of the sulfonyl function, and seldom are aprotic environments.[8] Consequently, some limitations arise such the inability to access some especially reactive sulfonyl halide derivatives.[9]

Sources of electrophilic halogen, such as the brominated and chlorinated derivatives of succinimide (NXS), are a practical option to carry out the oxidation of sulfur species for the generation of sulfonyl bromides and chlorides.[7e,7l] However, to our knowledge, there are no reports on the direct synthesis of the sulfonyl bromides or chlorides in a non-aqueous environment from thiols using *N*-bromo or *N*-chlorosuccinimide, and an alcohol as the oxygen source. Described below, is a novel, rapid and facile method for the generation of sulfonyl halides using ~~NXS (X=~~Br or Cl) as the oxidant and an alcohol as the oxygen source, allowing us to prepare several sulfonyl bromides and chlorides including examples that where not accessed with previously reported methods.

As part of our interest to revisit and develop methods based on sulfur functional groups,[10] we found that an alcohol additive provided a suitable environment for the generation of sulfonyl bromides. Early experimentation consisted in treating *p*-tolylmercaptan (**1a**) using a mixture of MeOH (2 equiv.) and *N*-bromosuccinimide (4 equiv.) in anhydrous dichloromethane. **1a** was cleanly converted into tosyl bromide (**2a**) with moderate isolated yield (Scheme 1).[11]



1a **2a** *(47%)*

Scheme 1. Early oxybromination system for the generation of sulfonyl bromide **2a** using NBS/MeOH.

We screened several different alcohols for the NBS/R-OH system to find the best reaction conditions (Table 1). *i*PrOH was chosen as the most suitable because the rate was improved substantially, whereas no alcoholic additive led to a poor transformation. Interestingly, an aromatic alcohol such as phenol was unable to promote the transformation giving instead the disulfide **4a**.[12] Further optimization, led to the decrease of the amount of oxidant in some cases (3.5 equiv., *vide infra*), without being detrimental to the performance of the transformation.

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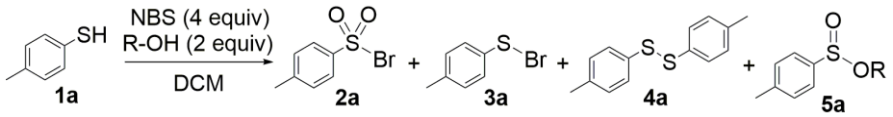
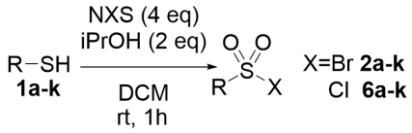
Table 1. Survey[a] of the alcohol component on the oxybromination of **1a**

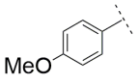
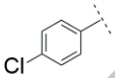
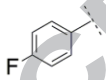
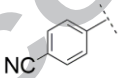
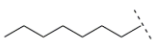


	Yields (%)[a]						
R-OH / t(min)	MeOH	*n*-BuOH	iPrOH	CyOH	tBuOH	PhOH	none
30	57%(**2a**) 43%(**5a**)	87%(**2a**) 13% (**5a**)	91% (**2a**) 9% (**3a**)	53%(**2a**) 47% (**4a**)	36%(**2a**) 64%(**3a**)	100% (**4a**)	6%(**2a**) 94%(**3a**)
60	78%(**2a**) 22%(**5a**)	94% (**2a**) 6% (**5a**)	**100% (2a)**	54%(**2a**) 46% (**4a**)	39% (**2a**) 61% (**3a**)	100% (**4a**)	6% (**2a**) 94% (**3a**)
120	84%(**2a**) 16%(**5a**)	95% (**2a**) 5% (**5a**)		54%(**2a**) 46% (**4a**)	50% (**2a**) 50% (**3a**)	100% (**4a**)	10%(**2a**) 90%(**3a**)

[a] ^{1}H-NMR yields.
[b] The reactions were conducted with 4 equivalents of NBS for 1 h, at rt.

Table 2. Substrate scope for the oxyhalogenation of thiols using the NXS/iPrOH system.



Entry[a]	R	X	Yield	
1		Br	72% **(2a)**	*c* 94%
2		Cl	70% **(6a)**	
3		F	**(7a)**	
4		Br	85% **(2b)**	
5[b]		Cl	94% **(6b)**	
6		Br	70% **(2c)**	
7		Cl	95% **(6c)**	
8		Br	77% **(2d)**	
9		Cl	80% **(6d)**	
10		Br	78% **(2e)**	
11		Cl	97% **(6e)**	
12		Br	68% **(2f)**	
13[b]		Cl	89% **(6f)**	
14		Br	74% **(2g)**	
15		Cl	99% **(6g)**	
16		Br	68% **(2h)**	*c* 59%
17		Cl	74% **(6h)**	
18		F	**(7h)**	
19		Br	73% **(2i)**	
20		Cl	99% **(6i)**	
21		Br	67% **(2j)**	
22[b]		Cl	56% **(6j)**	
23		Br	79% **(2k)**	
24[b]		Cl	85% **(6k)**	

[a] In the case of oxychlorinations, NCS should be added at 0 °C. [b] 3.5 equiv. of NCS were used. [c] TBAF (1.0 eq)/THF, 1h, rt.

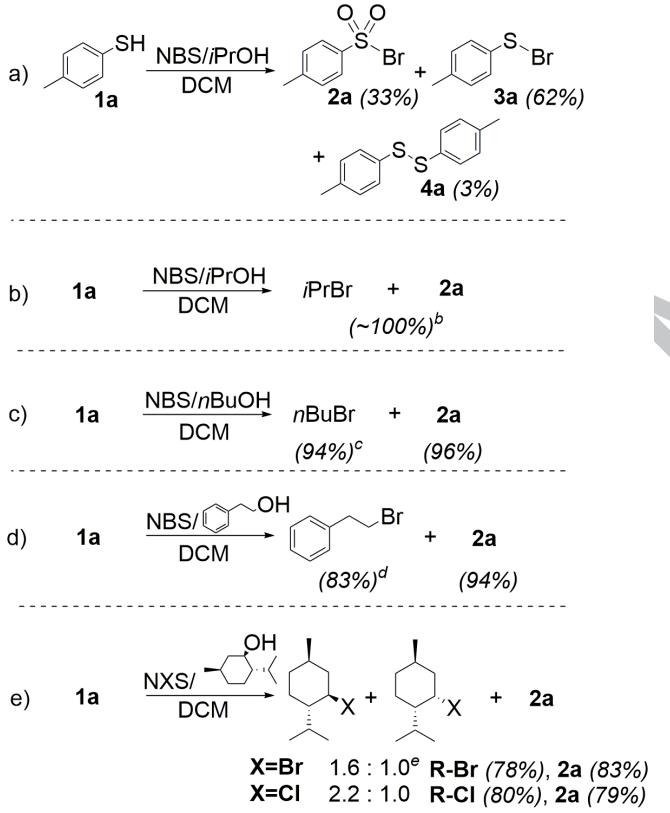
This was an improvement over previously reported NBS/NCS aqueous based methods where excessive equivalents of oxidant are needed,[7l,13] even with more oxidized sulfur derivatives such as disulfides.[9a]

With the optimal conditions at hand, we proceeded to expand the substrate scope with aromatic and aliphatic thiol precursors (Table 2). Swapping from NBS to NCS led to the corresponding sulfonyl chlorides, with virtually no change on the experimental conditions.[14] Varying the electronic nature of the thiols seems to have a low impact on the reaction efficiency (Table 2; entries 1-2, 4-15). In general, aliphatic substrates led to lower isolated yields (Table 2; entries 16-22), which reflects the volatility of some derivatives (e.g. **6j**). With this procedure, the oxybromination of benzyl mercaptan (**1h**) proceeded smoothly, leading to the sulfonyl bromide derivative **2h**, an elusive species that hasn't been reported previously.[9a] Sulfonyl bromides **2** are suitable for the preparation of sulfonyl fluorides **7** through a scarcely explored halogen replacement reaction using TBAF[15]. **2h** was easily transformed into the protease inhibitor PMSF[16] (phenylmethylsulfonyl fluoride, **7h**), and **2a** into **7a** efficiently (See Supplementary data). 1-heptanethiol **(1i)** was oxyhalogenated efficiently to yield 1-heptanesulfonyl bromide (**2i**), a relatively novel sulfonyl derivative.[9b] Substrates such as **2i** and **6i** are valuable since selected sulfur derivatives featuring long aliphatic chains, display enhanced fungicidal activity.[7f] In most instances, the prepared sulfonyl halides have long shelf lives if stored in a cold environment (-40 °C), except for **2h** and **2k**.[17]

Mechanistically, a disulfide **3** could be involved at early stages in the oxyhalogenation.[18] However, the oxyhalogenation of disulfides with the present method provided inferior yields. Treating the benzylic disulfide **3h** with the NBS/*i*PrOH reagent under standard conditions, led to a considerably slower and less effective transformation (27% yield of **2h**), with the recovery of an important amount of the starting disulfide. This result suggests, that the main pathway doesn't involve sulfenyl bromides **3** condensing with the starting thiols **1**, but rather **3** quickly evolving into oxygenated intermediates such as **8** when *i*PrOH is involved as the oxygen source (*vide infra*, Scheme 3). A control experiment where **1a** was exposed for a short period to the oxybromination reagent,[19] revealed disulfide **4a** in the reaction mixture as a trace (Scheme 2a), supporting a modest intermediacy of disulfides **4** in the mechanistic pathway.[20] To gain more insight into the reaction mechanism, we examined the crude reaction mixtures or representative experiments. ^{1}H-NMR of the untreated oxyhalogenation mixture of **1a** with NBS/iPrOH identified quantitatively isopropyl bromide and sulfonyl derivative **2a**, without any trace of isopropanol or **1a** (Scheme

2b). Also, inspection of the ^{1}H-NMR spectrum of crude mixture of the oxybromination of **2a** using NBS/*n*BuOH, revealed the presence of 1-bromobutane, without any trace of a rearranged substitution product such as isobutyl bromide (Scheme 2c). In the case of the NBS/phenethyl alcohol system, phenethyl bromide could be isolated after chromatography (Scheme 2d). The exclusive formation of these primary alkyl bromides led us to speculate that the alkyl halide generation from the activated sulfur species was primarily a concerted process. However, the kinetic evidence based on the reaction rates carried out with *n*BuOH and *i*PrOH, suggested a mixed mechanism in the latter case. This was confirmed with additional oxyhalogenation experiments of **1a** with NXS/L-menthol (Scheme 2e), where *uneven* ratios of the resultant diastereoisomeric menthyl bromides and chlorides suggested a contribution of a non-concerted substitution mechanism where a secondary alcohol was employed.[21]

Scheme 2. Control experiments[a] of oxyhalogenation of **1a** with iPrOH, nBuOH, phenethyl alcohol and L-menthol.

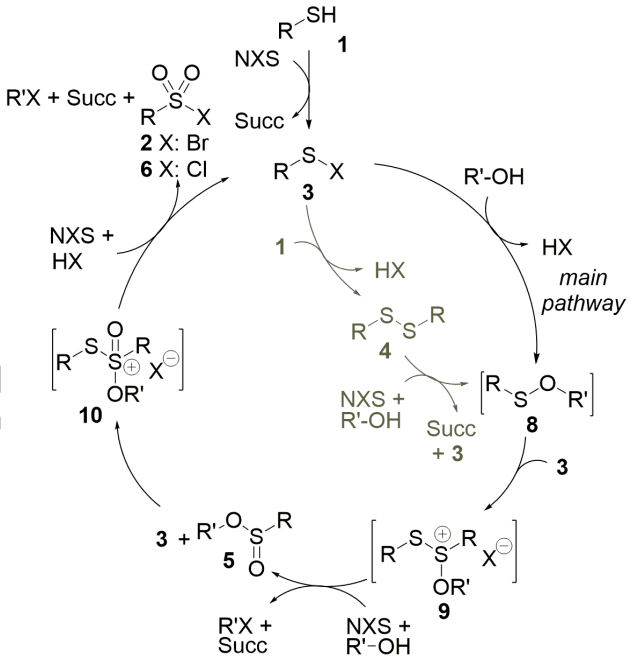


[a]Standard conditions were employed except for Scheme 2a where reaction time was 1 min. ^{1}H-NMR yields except for phenethyl bromide. [b]*i*PrBr detected on ^{1}H-NMR of the untreated reaction mixture. [c]nBuBr detected in the ^{1}H-NMR of the crude reaction mixture. [d]Isolated yield. [e]Diastereoisomeric menthyl bromides and chlorides were detected on ^{1}H-NMR of crude reaction mixtures.

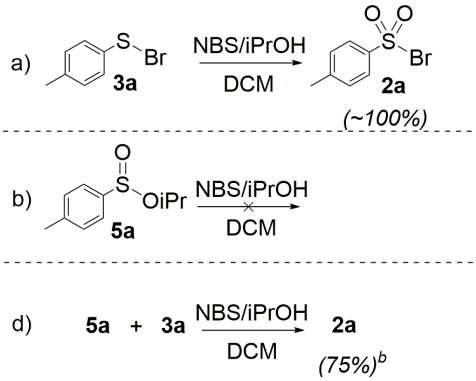
Based on these results, a plausible mechanism[22] is proposed in Scheme 3. Additional control experiments showed that **3a** suffered oxybromination under standard conditions (Scheme 4a). However, when sulfinate **5a** (R=*p*-tolyl, R'=*i*Pr) was exposed to the oxybromination mixture, unreacted material was obtained (Scheme 4b). We speculated that the sulfinate intermediary **5** could only evolve in the presence of sulfanyl halide **3**, because of its high electrophilicity and consequently activating role. Therefore, we exposed sulfinate **5a** to the oxybrominating mixture NBS/*i*PrOH in the presence of sulfanyl bromide **3a**, leading to a 4:1 ratio of sulfonyl bromide **2a** and sulfinate **5a** respectively, consistent with the involvement of sulfinates **5** as intermediaries.

A collection of aryl/alkyl sulfonyl bromides and chlorides were prepared from thiols (**1**) through a facile oxyhalogenation reaction. Challenging sulfonyl bromides, such as **2h** and **6i** could be prepared swiftly, meanwhile other novel sulfonyl bromides (**2f**, **2i-k**) and know sulfonyl bromides and chlorides (**2a-e,g,h** and **3a-k**) were also prepared efficiently. Bromosulfonyl derivatives (**3**) can be used for the generation of sulfonyl fluorides such as **7b** or **7h,** by means of a TBAF nucleophilic displacement. The new procedure can be performed if desired under anhydrous conditions, and is effective with both aliphatic and aromatic substrates without influence from the electronic nature of substrate.

Scheme 3. Mechanistic proposal



Scheme 4. Additional control experiments[a]



[a]Standard conditions were employed. ^{1}H-NMR yields. [b] Yield was estimated considering both **5a** and **3a**. ~25% of **5a** was identified in the reaction mixture.

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19. The reaction mixture was quenched after 1 min of adding the oxidant.
20. See the Supplementary data for additional control experiments.
21. a) At this point we cannot support the formation of a carbocation intermediate, since we could not detect any tertiary chloride product, which is expected if an intermediate of this nature was involved within the mechanism (see Mondal, D.; Li, S. Y.; Bellucci, L.; Laino, T.; Tafi, A.; Guccione, S.; Lepore, S. D. *J. Org. Chem.* **2013**, *78*, 2118-2127). b) The possibility of an ion pair has also been postulated for similar displacements (see Braddock, D. C.; Pouwer, R. H.; Burton, J. W.; Broadwith, P. *J. Org. Chem.* **2009**, *74*, 6042-6049).
22. A related mechanism, where an alcohol is the source of oxygen for generation of sulfonyl chlorides from benzyl aryl thioethers has been reported, see ref. 13.

Supplementary Material

Supplementary data, such as experimental details including procedures, characterization, and spectra data, can be found in the online version at http://dx.doi.org/xxxxxx

Sulfonyl halide synthesis by thiol oxyhalogenation using NBS/NCS - *i*PrOH

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Highlights:

- A novel oxyhalogenation of thiols to yield sulfonyl bromides and halides efficiently
- Method suitable for the preparation of challenging sulfonyl halides
- NXS/*i*PrOH as a novel oxyhalogenation reagent (X: Br or Cl)
- *i*PrOH serves as the source of oxygen

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