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Synthesis of allyl sulfones from potassium allyltrifluoroborates

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ABSTRACT

Potassium allyltrifluoroborates underwent a bora-*ene* reaction with sulfur dioxide in the absence of Lewis acid catalysts to give sulfinyloxy-trifluoroborates, which subsequently undergo alkylation with electrophiles to produce sulfones in up to 91% yield. Benzyl halides and haloacetic acid derivatives can be used as the alkylation reagents while the Sanger reagent undergoes a S_NAr reaction with sulfinyloxy-trifluoroborates to produce the corresponding 2,4-dinitrophenylsulfone. The developed method allows the transformation of potassium allyltrifluoroborates into allyl sulfones.

Sulfones are regarded as a very useful class of compounds[1] that have many important applications in medicinal chemistry,[2] agrochemistry,[3] and materials science.[4] Sulfones also possess distinct chemical reactivity and as such have been successfully used as synthetic intermediates. Named reactions including the Julia-Kocienski olefination[5] and Ramberg-Bäcklund reaction,[6] the use of vinyl sulfones as Michael acceptors,[7] and the applications of sulfone-stabilized carbanions,[8] are representative illustrations for the synthetic utility of sulfones.

Recent advances in the synthesis of sulfones have been reviewed.[8b,9] A well-accepted method is alkylation of the corresponding sulfinate salts, which can be obtained by reacting various organometallic reagents with sulfur dioxide or its solid surrogates. Contemporary synthetic pathways developed until 2015 and dealing with the insertion of SO_2 into carbon-heteroatom bonds, including reactions of aryl and vinyl halides, alkoxysilanes, and boronic acids in the presence of transition metal catalysts, have also been reviewed (Fig. 1. Part 1).[9a] In 2016, aryl nonaflates were also reported to yield sulfinates in a palladium catalyzed reaction with sulfur dioxide.[10] Other very recent achievements regarding the fixation of SO_2 into small organic molecules are sulfone synthesis *via* copper(I) oxide[11] and cobalt(II) oxide[12] catalyzed SO_2 insertion into aryl triethoxysilanes. Also, copper(I)[13] and palladium(II)[14] catalyzed processes were developed for the transformation of aryl and alkenyl boronic acids into sulfinates and subsequently into sulfones. The fixation of SO_2 into cyclic sulfones, benzo[*b*]thiophene 1,1-dioxides, was achieved by reacting the former with 2-alkynylaryldiazonium in the presence of catalytic CuBr.[15] On the other hand, advancing the field of late transition metal free processes has led to the iron-catalyzed synthesis of arylsulfinates through a radical coupling reaction[16] and photo-induced fixation of sulfur dioxide into aryl/alkyl halides.[17]

From the above mentioned methods for the synthesis of sulfinate intermediates,[18] one can separate the reactions of allylic systems with SO_2 (Fig. 1. Part 2). Thus, procedures involving allylmagnesium halides, allylmanganese,[19] allyliron,[19,20] allylplatinum,[21] and allylpalladium[22] derivatives are known. Also, less reactive allylsilanes react with SO_2 under Lewis acid catalysis.[23] On the other hand, allylic systems possessing intrinsic Lewis acidity such as allylboronates[24] and allylstananes[25] react in the absence of any catalyst. Besides the discussed metallo-*ene* reactions,[26] H-*ene* reactions of simple allylic systems with SO_2 are also known. These require activation with BCl_3 and produce sulfinic acid–BCl_3 complexes.[27] These achievements are due to a renaissance of the use of sulfur dioxide and its solid surrogates as reagents[28] and liquid sulfur dioxide as a solvent[29] in organic synthesis.

To the best of our knowledge, the reactions of potassium allyltrifluoroborates with sulfur dioxide have not been described. Herein, we report the synthesis of potassium 3-((allylsulfinyl)oxy)trifluoroborates *via* the bora-*ene* reactions between potassium allyltrifluoroborates and SO_2, and their application in sulfone synthesis.

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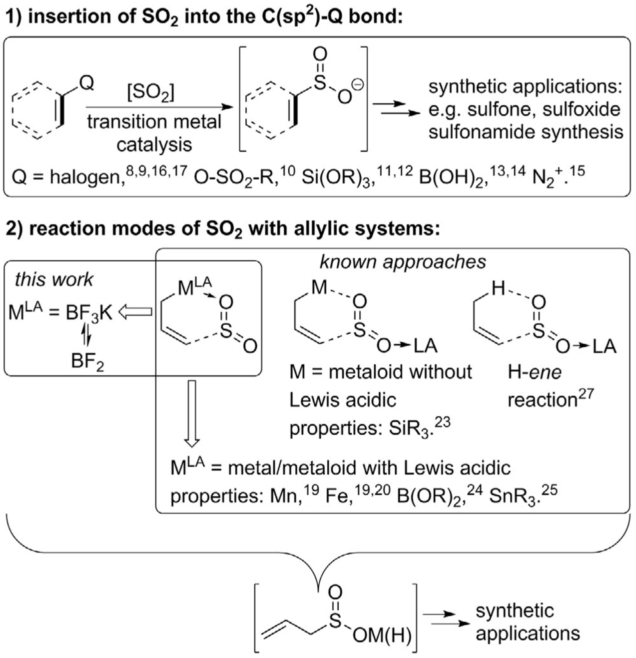
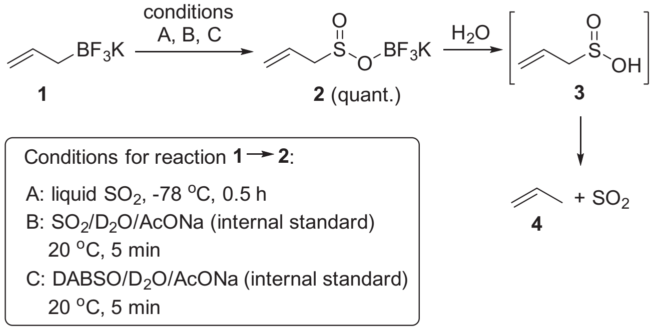


Fig. 1. Examples of SO_2 incorporation into organic compounds.



Scheme 1. Synthesis and stability studies of potassium 3-((allylsulfinyl)oxy) trifluoroborate (**2**).

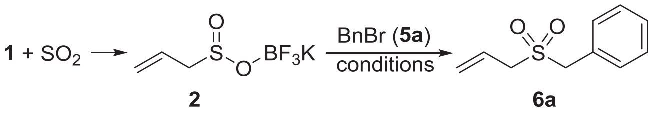
Commercially available potassium allyltrifluoroborate (**1**) readily reacts with sulfur dioxide at -78 °C to give potassium 3-((allylsulfinyl)oxy)trifluoroborate (**2**) (Scheme 1). Sulfur dioxide serves as both the reagent and solvent, and the addition of a catalyst to promote the reaction is not required. After the removal of SO_2, product **2** is obtained as a white paste in quantitative yield, which was determined by ^1H NMR analysis of the crude product in the presence of sodium acetate as an internal standard. Similar results were obtained by adding either D_2O saturated with gaseous SO_2 or the 1,4-diazabicyclo[2.2.2]octane bis(sulfur dioxide) adduct (DABSO)[14a] to a solution of starting material **1** and sodium acetate (internal standard) in D_2O. ^1H NMR analysis of the latter solutions revealed instant and quantitative formation of product **2**.

During the characterization of compound **2** we observed its variable stability which was dependent on the solvent used. Tests were carried out using ^1H NMR and 2-bromomesitylene (for organic solvents) or sodium acetate (for aqueous solutions) as internal standards. Sulfinyloxy trifluoroborate **2** is reasonably soluble in water and is stable for at least 12 h at ambient temperature. In contrast, it is less soluble in wet DMSO, but still stable at ambient temperature. However, it is less stable in wet DMSO at elevated temperatures (80 °C) and degrades to propene (**4**, observed by ^1H NMR) and SO_2, apparently through a *retro-ene* elimination from the intermediate allylsulfinic acid (**3**).[30,31] Finally, it was found that the addition of DMF to the aqueous solution of **1** does not influence its stability and such solutions are stable for at least 24 h, even at slightly elevated temperatures (60 °C).

With these results in hand we turned our attention to the alkylation of *in situ* generated potassium 3-((allylsulfinyl)oxy)trifluoroborate (**2**). Benzyl bromide (**5a**) was chosen as a model electrophile and several experimental conditions were screened by varying solvent systems, bases and temperatures (Table 1). It was found that the alkylation proceeded poorly under non-aqueous conditions (Table 1, entries 1–3), most probably due to the low solubility of intermediate **2**. Use of the biphasic systems H_2O/DCM and H_2O/MeCN also did not improve the yields (Entries 4–5). This information regarding the stability of intermediate **2** and its solubility led to use of the H_2O/DMF (1:1) solvent system (Entries 6–11). Initially the alkylation was attempted at 20 °C and 40 °C in the absence of additional base since intermediate **2** formally represents a sulfinate salt (Entries 6–7). Improved yields for the synthesis of sulfone **6a** was achieved after the examination

Table 1

Optimization of the reaction conditions for the synthesis of sulfone **6a** using *in situ* generated potassium 3-((allylsulfinyl)oxy)trifluoroborate **2**.[a]



Entry	Base	Solvent	Temp. (°C)	Time (h)	Product **6a** (%)
1	–	DMF	20	28	16[b]
2	–	DMF	40	23	13[b]
3	K_2CO_3	DMSO	20	22	25[b]
4	NaOH	H_2O/DCM	20	20	4[b]
5	–	H_2O/MeCN	20	7	7[b]
6	–	H_2O/DMF	20	23	23[b]
7	–	H_2O/DMF	40	22	28[b]
8[c]	KF	H_2O/DMF	20	27	32[d]
9[c]	K_2CO_3	H_2O/DMF	20	27	**62**[d]
10[c]	NaOAc	H_2O/DMF	20	24	**64**[d]
11[c]	NaOH	H_2O/DMF	20	25	**77**[d]

[a] Reagents and conditions: **1** (0.22 mmol), RX (0.27 mmol, 1.2 equiv.), base (0.4 equiv.), solvent (2.0 mL, 1:1 ratio for entries 4–11), rt, 24 h.

[b] ^1H NMR yield, internal standard: diphenylmethane.

[c] TBAI (10 mol%).

[d] Isolated yield (numbers in bold are provided for the optimal reaction conditions).