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One-pot Synthesis of Allyl Sulfides from Sulfinate Esters and Allylsilanes through Reduction of Alkoxysulfonium Intermediates

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An efficient method to synthesize allyl sulfides from sulfinate esters and allylsilanes is described. Based on the reactivity of isolated allyl(methoxy)phenyl triflate, we have developed a simple one-pot method for the allyl sulfide synthesiss by *S*-allylation of sulfinate esters and subsequent reduction with sodium borohydride. A number of allyl sulfides were prepared by this method keeping various functional groups unreacted.

Keywords: Sulfide, Sulfinate ester, Alkoxysulfonium

Organosulfur compounds have played important roles in broad disciplines including not only organic chemistry but also pharmaceutical sciences, materials chemistry, and chemical biology.[1,2] Particularly, allyl sulfides have gained attention due to their synthetic versatility.[3] A wide range of transformations of allyl sulfides have been reported such as thiol-ene reaction,[3d,3g] olefin cross-metathesis,[3c] catalytic allylthiolation of alkynes,[3b] and insertion reactions with diazo compounds through [2,3]-sigmatropic rearrangement[3a,3h] catalyzed by rhodium, copper, and so on (Figure 1A). In general, allyl sulfides are synthesized by *S*-allylation of thiols (Figure 1B). However, accessible allyl sulfides are still limited due to stinking, oxidizable, and highly nucleophilic thiols. Herein, we describe a novel method to prepare allyl sulfides by *S*-allylation of sulfinate esters and subsequent reduction of the resulting alkoxysulfonium intermediates.

Alkoxysulfonium salts[4,5] are well-known intermediates in the Swern oxidation, in which carbonyl compounds are prepared from alcohols with dimethyl sulfoxide, oxalyl chloride, and triethylamine at low temperature.[6] Pioneering studies on reactivities of alkoxysulfonium salts isolated were reported by Jonson and Phillips in the 1960s.[4a–c] For example, *O*-methylation of sulfoxides with trimethyloxonium tetrafluoroborate provided a limited number of methoxysulfonium salts, which smoothly reacted with sodium borohydride to afford sulfides.[4c] In 1974, Durst and coworkers reported the reduction using sodium cyanoborohydride with 18-crown-6 instead of sodium borohydride.[4d] Although several sulfides were efficiently synthesized from alkoxysulfonium salts, the harsh conditions preparing alkoxysulfonium salts using the highly electrophilic alkylating reagent have hitherto limited the synthetic utility.

In the course of our studies on organosulfur chemistry,[7] the recent success of allyl sulfoxide synthesis from sulfinate esters[8] motivated us to revisit the alkoxysulfonium salt chemistry.[9] Indeed, we recently found that the interrupted Pummerer-type reaction of sulfinate esters **1** using trifluoromethanesulfonic anhydride (Tf_2O)[10,11] in the presence of allylsilanes **2** efficiently afforded allyl sulfoxides through alkoxysulfonium intermediates **4** (Figure 1C).[8] In this recent study, we succeeded in the isolation of allyl(methoxy)phenylsulfonium triflate (**4a**) by avoiding aqueous work-up. Since sodium borohydride reduction of **4a** furnished allyl phenyl sulfide (**5a**), we decided to examine the reactivity of **4a** to establish the allyl sulfide synthesis from sulfinate esters **1** (Figure 1D).

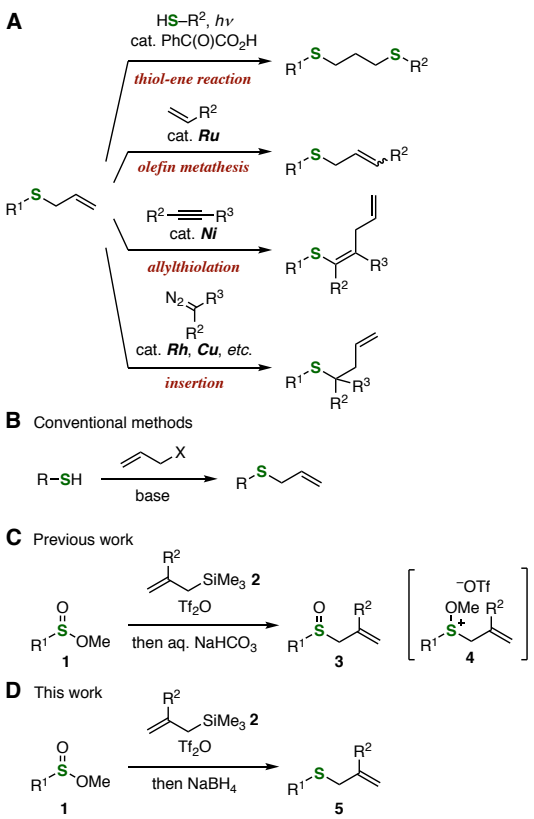
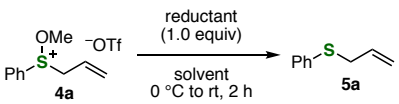


Figure 1. Background and overview of this study. (A) Transformations of allyl sulfides. (B) Conventional allyl sulfide synthesis. (C) Our previous work. (D) This work.

We first screened a variety of conditions for the reduction of alkoxysulfonium salt **4a** (Table 1). As a result, although the reaction in methanol afforded sulfide **5a** in high yield (entry 1),[8] changing the solvent to ethanol, tetrahydrofuran (THF), or dichloromethane significantly

decreased the yield of sulfide **5a** (entries 2–4). Adding 18-crown-6 or 15-crown-5 slightly improved the efficiency of the reduction in dichloromethane (entries 5 and 6). According to the reported conditions by Durst and coworkers,[4d] reduction of **4a** with sodium cyanoborohydride in methanol proceeded smoothly (entry 7). Sulfide **5a** was also obtained in moderate yields by the reduction using sodium cyanoborohydride with 18-crown-6 or 15-crown-5 in dichloromethane (entries 8 and 9). When sulfonium salt **4a** was treated with lithium borohydride, sulfide **5a** was obtained in low yield (entry 10). The reaction of **4a** with lithium aluminum hydride or diisobutylaluminum hydride also proceeded, although the yields of **5a** were low (entries 11 and 12). In addition, triethylsilane and 1,4-cyclohexadiene were ineffective to reduce sulfonium salt **4a** (entries 13 and 14).

Table 1. Screening of reducing conditions



Entry	Reductant	Solvent	Yield/%[a]
1[b]	$NaBH_4$	MeOH	80
2	$NaBH_4$	EtOH	37
3	$NaBH_4$	THF	20
4	$NaBH_4$	CH_2Cl_2	15
5	$NaBH_4$ + 18-crown-6	CH_2Cl_2	36
6	$NaBH_4$ + 15-crown-5	CH_2Cl_2	31
7	$NaBH_3CN$	MeOH	78
8	$NaBH_3CN$ + 18-crown-6	CH_2Cl_2	57
9	$NaBH_3CN$ + 15-crown-5	CH_2Cl_2	55
10	$LiBH_4$	MeOH	27
11	$LiAlH_4$	THF	36
12	*i*-Bu_2AlH	THF	29
13	Et_3SiH	THF	0
14	1,4-cyclohexadiene	CH_2Cl_2	0

[a] ^{1}H NMR yields. [b]Data from ref. 8.

To gain insight into the reactivity of sulfonium salt **4a**, we performed a theoretical calculation of **4a** (Figures 2A and 2B). As a result, the LUMO of the optimized structure showed a large coefficient at the sulfur atom, suggesting the electrophilic nature at the sulfonium sulfur. In addition, ^{1}H NMR analysis of sulfonium salt **4a** in methanol-d_4 showed that most of sulfonium salt **4a** was observed without incorporation of trideuteriomethoxy group after stirring for 10 min, and **4a** completely decomposed after 24 h. This result indicated that cleavage of S–O bond resulting to exchange the methoxy group with the solvent did not proceed in the protic solvent and sulfonium salt **4a** slowly decomposed in methanol.[12]

A deuteration experiment using $NaBD_4$ afforded deuterium-free sulfide **5a** showing that deprotonation of sulfonium salt **4a** did not take place despite the presence of highly acidic allylic proton of **4a** (Figure 2C). This result strongly supports the plausible reaction mechanism shown as path A in Figure 2D; substitution reaction at the sulfonium sulfur with hydride ion and subsequent deprotonation lead to sulfide **5a**, similar to the pioneering study using methyl(methoxy)phenylsulfonium tetrafluoroborate.[6c] On the other hand, the mechanism shown as path B in Figure 2D is excludable, since the deprotonation was not observed in the deuteration experiment (Figure 2C).

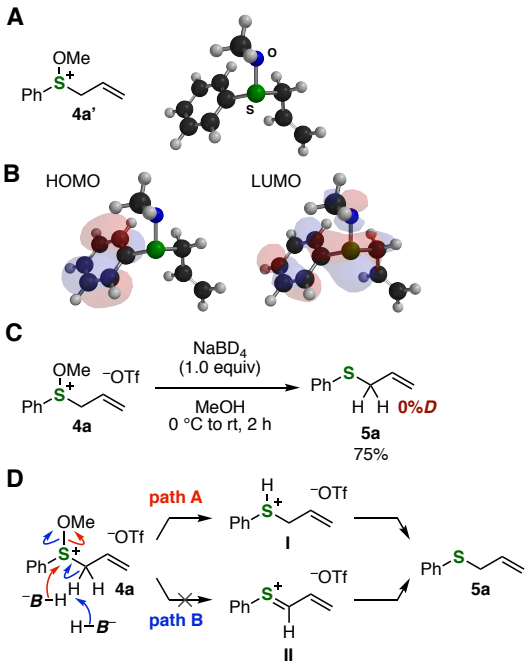
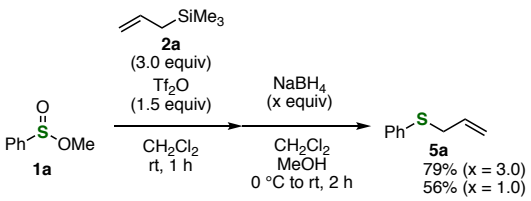


Figure 2. Examination of the reactivity of alkoxysulfonium salt **4a**. (A) Optimized structure of sulfonium salt **4a'** using a DFT method (B3LYP/6-311G(d,p)). (B) HOMO (left) and LUMO (right). (C) Deuteration experiment. (D) Possible reaction pathways.

We then turned our attention to achieve the allyl sulfide synthesis by performing the *S*-allylation and subsequent reduction in a one-pot manner (Scheme 1). As a result, treatment of sulfinate ester **1a** and allyltrimethylsilane (**2a**) with Tf_2O followed by the addition of methanol and sodium borohydride (3.0 equiv) provided sulfide **5a** in good yield. Reducing the stoichiometry of sodium borohydride to 1.0 equiv resulted in a decrease of the yield.



Scheme 1. One-pot synthesis of allyl sulfide **5a** from sulfinate ester **1a** and allylsilane **2a**.

A wide variety of allyl sulfides were successfully prepared by the one-pot method (Figure 3). Indeed, allyl sulfide **5b** was synthesized from electron-deficient methyl *p*-chlorophenylsulfinate in excellent yield. Naphthylsulfinate ester also participated in this reaction to afford allyl sulfide

5c. Moreover, the reaction of bulky substrate such as methyl *o*-bromophenylsulfinate uneventfully proceeded to afford sulfide **5d**. The Pummerer-type allylation of sulfinate ester **1a** with 2-phenylpropenyl(trimethyl)silane followed by the reduction also smoothly took place to afford sulfide **5e** bearing a substituent on the alkene moiety. It is worth noting that allyl sulfides **5f** and **5g** having chloro and acetoxy groups, respectively, at the allylic position were synthesized in good yields keeping these groups with high leaving-group ability intact. Since allyl sulfides are generally prepared from thiols and allyl halides, these results clearly showed an advantage of the present method for preparing allyl sulfides bearing leaving groups.

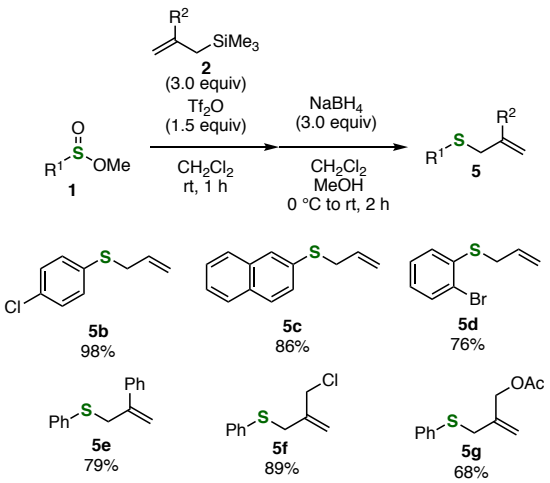


Figure 3. Synthesis of various allyl sulfides from sulfinate esters and allylsilanes.

In summary, we have developed a facile method to synthesize allyl sulfides from sulfinate esters and allylsilanes. On the basis of a number of examinations using alkoxysulfonium salt **4a**, an efficient one-pot procedure by *S*-allylation and the following reduction was established. Further studies to examine the scope and limitations of the method and application to the synthesis of bioactive organosulfur compounds are now underway.

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Supporting Information is available on http://dx.doi.org/10.1246/cl.xxxxxx.

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12 A complex mixture involving allyl phenyl sulfoxide was observed by the decomposition.