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The Reactions of 2-(Trimethylsilyl)ethyl Benzenesulfenate as an Equivalent of Sulfenate Anion or a Precursor of Sulfenyl Cation

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The reaction of 2-(trimethylsilyl)ethyl benzenesulfenate was investigated. In the reaction of the sulfenate with alkyl halide, it was found that the sulfenate behaved as an equivalent of sulfenate anion to give sulfoxides under the catalytic action of potassium fluoride on calcium fluoride. In the presence of trimethylsilyl trifluoromethanesulfonate, olefin, and acetonitrile, it was found that the sulfenate behaved as a precursor of sulfenyl cation to afford episulfonium cation intermediate, which reacted with acetonitrile to give amidosulfonylation products.

KEY WORDS: Reaction of 2-(Trimethylsilyl)ethyl Benzenesulfenate / Equivalent of Sulfenate Anion / Synthesis of Sulfoxides / Potassium Fluoride on Calcium Fluoride / Precursor of Sulfenyl Cation / Benzenesulfonyl Trifluoromethanesulfonate / Episulfonium Cation / Amidosulfonylation of Olefin

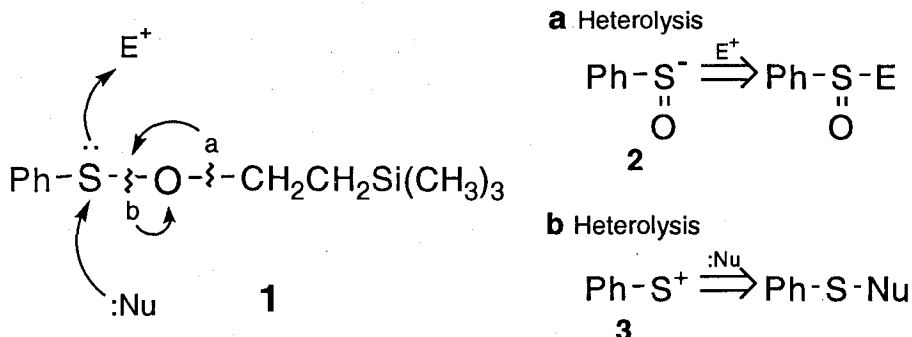
Sulfonic acid and sulfinic acid are versatile reagents for organic chemistry. On the contrary, sulfenic acid which is one of series of these sulfur-containing acids and well-known compound as a product of sulfoxide elimination¹⁾, have been scarcely investigated for organic synthesis²⁾, because sulfenic acid is very unstable and have not been isolated with few exceptions³⁾.

In our previous paper⁴⁾, it was reported that 2-(trimethylsilyl)ethyl benzenesulfenate (**1**) was reacted with several alkyl or alkenyl halides in the presence of anhydrous tetrabutylammonium fluoride (TBAF) to give sulfoxides. These reactions clearly showed us **1** is a useful reagent as an equivalent of sulfenate anion **2**.

TBAF is a well-known reagent as a source of fluoride anion. A solution of TBAF in THF is commercially available, but the solution contains 5% H₂O as a stabilizer. If an anhydrous conditions are desirable, it is necessarily to dry the solution over molecular sieves. Recently, it was reported by Ando et al.^{5a)} and Clark et al.^{5b)} that potassium fluoride carried on calcium fluoride (KF/CaF₂) is a more convenient fluoride anion source for halide-fluoride exchange of alkyl halide than that of TBAF,

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Scheme 1

because KF/CaF_2 is prepared without any difficulties.

In this paper, we wish to report reactions of **1** with alkyl halides using KF/CaF_2 as a catalyst, and amidosulfenylation of olefin with **1** in the presence of trimethylsilyl trifluoromethanesulfonate (TMSOTf) and acetonitrile. In these reactions, **1** would be an equivalent of sulfenate anion (**2**) and a precursor of sulfenyl cation (**3**), respectively. It was reasonable expected that the sulfur atom of **1** would have dual reactivities toward nucleophile and electrophile (Scheme 1).

Reaction of **1** as an Equivalent of Sulfenate Anion

The reaction of **1** with benzyl bromide or cinnamyl bromide was carried out in the presence of KF on CaF_2 to give sulfoxides, **5**, and the results were summarized in Table 1. The reaction were hardly proceeded in THF at room temperature (run 1 in Table 1), while under similar conditions using TBAF the reaction underwent smoothly as shown in eq. 1⁴). In dichloroethane at higher temperature, the yield of **5** was improved to 68% (run 3 in Table 1). In this reaction, benzyl phenyl sulfide, **6** and butyl phenyl sulfide were not detected, while both of the sulfides were obtained in 8% and 15%, respectively, when TBAF was employed as a fluoride source (eq. 1)⁴).

A possible reaction pathway for the reactions is proposed as shown in Scheme 2. The desilylation of **1** with fluoride and consecutive elimination of ethylene might produce sulfenyl anion, **2** (path a). This pathway is analogous to the generation of carboxylate anion from 2-trimethylsilylethyl ester⁶). More plausible pathways are as follows; the alkylation of sulfur of **1** with alkyl halide would be proceeded to give oxysulfonium salt, **4**, as an intermediate. At this stage, the silyl group of **4** would be more readily removable so that **4** would be attacked by fluoride anion at silyl group to yield **5** (path b). When soluble TBAF was used instead of KF/CaF_2 , the α -hydrogen of oxygen atom in **4** was abstracted by fluoride anion to afford the undesirable product, sulfide **6** in a manner similar to

The Reaction of 2-(Trimethylsilyl)ethyl Benzenesulfonate

Table 1

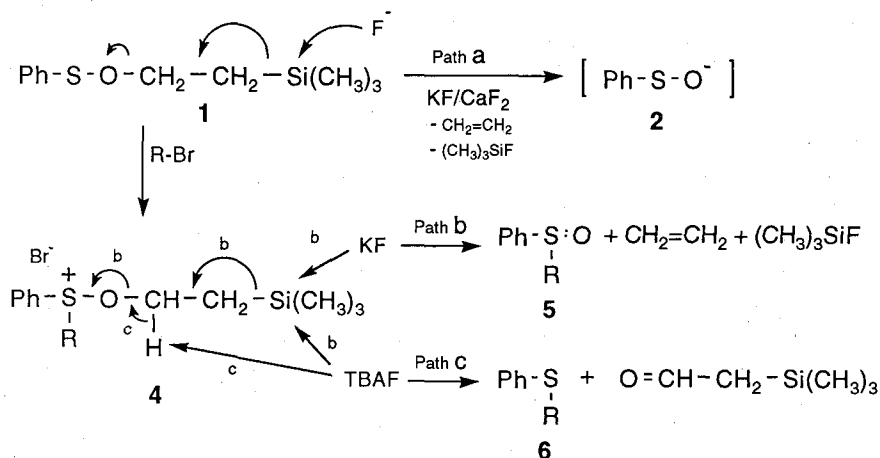
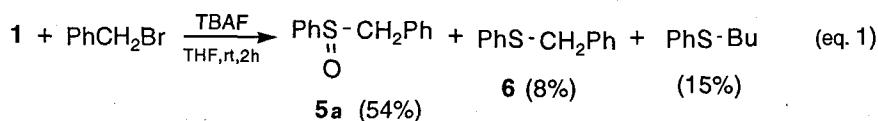
$$1 + \text{R-Br} \xrightarrow{\text{KF/CaF}_2^{\text{a)}}} \text{Ph-S-R}$$

$$\begin{array}{c} \parallel \\ \text{O} \end{array}$$

5a ; R=CH₂Ph
b ; R=CH₂CH=CHPh

run	R-Br	Conditions			Yield of 5
		solvent	temp.	time	
1	PhCH ₂ Br	THF	rt	2h	0
2	PhCH ₂ Br	THF	reflux	72h	19%
3	PhCH ₂ Br	ClCH ₂ CH ₂ Cl	reflux	20h	68%
4	PhCH=CHCH ₂ Br	ClCH ₂ CH ₂ Cl	reflux	16h	62%

a) 2 equiv. of KF (10 weight% on CaF₂) based on 1 was used.

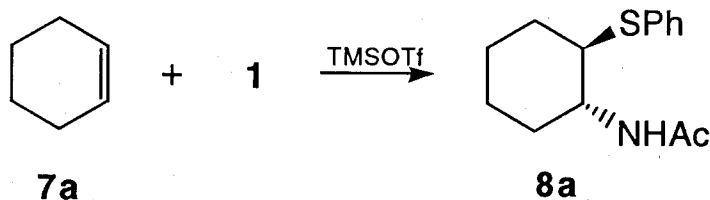


Swern oxidation (path c), because TBAF is more basic than insoluble KF/CaF₂.

Reaction of 1 as a Precursor of Sulfenyl Cation

In the presence of cyclohexene (7a) and acetonitrile, the reaction of 1 with trimethylsilyl trifluoromethanesulfonate (TMSOTf) was carried out under a variety of conditions to obtain an amidosulfonylation product of cyclohexene, 1-acetylamino-2-phenylthiocyclohexane (8a) (see Table 2). It gave more satisfactory results

Table 2



run	Conditions			Yield of 8a
	solvent	temp.	time	(%)
1	CH ₃ CN,	0°C→rt	45h	25
2	CH ₃ CN,	reflux,	2h	16
3	CH ₃ CN,	-70°C→0°C,	2h	40
4	CH ₂ Cl ₂ ,	-30°C,	2h	12
5	CH ₂ Cl ₂ ,	-30°C→rt,	24h	36
6	CH ₂ Cl ₂ ,	reflux,	4h	28
7	ether,	-30°C→rt	24h	4

when TMSOTf was added while the reaction mixture was kept cool (ca. -30°C) and then allowed it warm up to room temperature (compare with run 1 vs 3 and 4 vs 5 in Table 2). Using CH₂Cl₂ as a solvent and an equimolar amount of acetonitrile, the almost same results were obtained to that of CH₃CN as a solvent (see run 3 and run 6 in Table 2). In this reaction, it was enough to use only an equimolar amount of nitrile.

The reaction would be initiated by silylation of oxygen atom at **1** with TMSOTf to yield oxonium salt, **9**, which was easily rearranged to trimethylsilyl benzenesulfenate (**10**), TMSOTf, and ethylene (Scheme 3). In a similar manner to that of **9**, **10** was also reacted with TMSOTf to give benzenesulfonyl trifluoromethanesulfonate (**12**) via oxonium salt, **11**. The silyl sulfenate, **12** should be highly reactive sulfonyl cation source⁷, and underwent electrophilic addition to **7a** to afford the episulfonium cation (**13**)⁸. The counter anion, triflate is so poor nucleophile that **13** should be a free ion and very reactive toward acetonitrile in Ritter type reaction to give **8a**. A similar reaction course as shown in Scheme 3 was proposed for the amidoselenation⁹. In a NMR spectrum, the coupling constant between 1-H and 2-H was 10.5 Hz which indicated that both hydrogens were in axial. The result was an additional evidence for the reaction mechanism in Scheme 3.

In the reaction of 1-decene (**7**), a mixture of Markownikoff adduct, **8b** and anti-Markownikoff adduct, **8b'** (the ratio of **8b/8b'** is 13/1) was isolated in a poor yield (eq. 2). A similar reaction of **1** was carried out in the presence of benzyl carbamate instead of CH₃CN in CH₂Cl₂, and an unexpected product, white crystalline oxysulfonylation compound (**8c**) precipitated out from the reaction mixture (eq. 3), while an expected amidosulfonylation product (**8c'**) did not detect in the reaction mixture. It was found that **8c** underwent a rearrangement to **8c'** under

acidic conditions in dioxane containing a catalytic amount of conc-HCl, in which **8c** was soluble (eq. 4). Probably **8c** would be a kinetically controlled product.

In conclusion, it was found that the reaction of **1** with alkyl halide catalyzed by KF/CaF₂ provided one of a convenient routes for preparation of sulfoxides without oxidizing agents, while in the presence of TMSOTf, **1** should be a good reagent for the generation of benzenesulphenyl cation. It was clearly shown that **1** had dual characters of an equivalent of benzenesulfenate anion and a precursor of benzenesulphenyl cation.

Experimental

¹H NMR spectra were recorded on a GE QE-300 spectrometer (300MHz) in CDCl₃ with tetramethylsilane as an internal standard. Mass spectra were obtained on a Hitachi M-80B spectrometer. KF/CaF₂ was prepared by the methods of Ando and his co-workers^{5a}. Benzyl bromide, cinnamyl bromide, and solvents such as CH₂Cl₂, CH₂ClCH₂Cl, THF, and CH₃CN were distilled over CaH₂ or sodium benzophenone ketyl.

Reaction of 1 with Benzyl Bromide in the Presence of KF/CaF₂. KF/CaF₂ (10 weight% of KF on CaF₂, 0.58 g, 1.0 mmol) was activated by drying under 2 mmHg for 1 h. To a suspension of the KF/CaF₂ in 1,2-dichloroethane (4 ml) was added **1** (0.11 g, 0.48 mmol) and benzyl bromide (0.30 ml, 2.5 mmol) under N₂. The resulting mixture was stirred under reflux for 20 h. After filtration and concentration, the residue obtained was chromatographed on silica gel (hexane/EtOAc, 1/1) to afford **5a** (R = CH₂Ph 70 mg, 68%): ¹H NMR δ 3.98 (d, 1H, J=12 Hz), 4.10 (d, 1H, J=12 Hz), 6.95-6.99 (m, 2H), 7.24-7.27 (m, 3H), 7.35-7.45 (m, 5H); MS m/e 216 (M⁺).

5b (R = CH₂CH=CHPh): ¹H NMR δ 3.64 (ddd, 1H, J=1, 8, 16 Hz), 3.70 (ddd, 1H, J=1, 2, 8 Hz), 5.97 (dt, 1H, J=8, 16 Hz), 6.41 (dt, 1H, J=1, 16 Hz), 7.21-7.29 (m, 5H), 7.43-7.64 (m, 5H); MS m/e 242 (M⁺).

Reaction of 1 with 8a and Acetonitrile in the Presence of TMSOTf. To a cold (-30°C) solution of **1** (0.23 g, 1.0 mmol), **8a** (0.20 ml, 2.0 mmol), and acetonitrile (0.16 ml, 3.0 mmol) in CH₂Cl₂ (2 ml) was added TMSOTf (0.23 ml, 1.1 mmol). The mixture was allowed to warm up to rt under stirring. After 24 h, reaction mixture was poured into saturated aqueous NaHCO₃ (20 ml) and extracted with ether (3×15 ml). The ethereal extracts were washed with water (20 ml) and brine (20 ml), dried over MgSO₄, and concentrated under reduced pressure. The residue obtained was chromatographed on silica gel (EtOAc) to afford **8a** (0.090 g, 36%): ¹H NMR δ 1.2-1.5 (m, 4H), 1.6-1.7 (m, 2H), 1.88 (s, 3H), 2.0-2.2 (m, 2H), 2.91 (dt, 1H, J=4, 11 Hz), 3.75 (dt, 1H, J=4, 11 Hz), 5.7-5.9 (m, 1H), 7.2-7.5 (m, 5H); MS m/e 250 (M⁺+1).

8b: ¹H NMR δ 0.86 (t, 3H, J=7 Hz), 1.2-1.7 (m, 14H), 1.83 (s, 3H), 3.09 (d, 1H,

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J=5 Hz), 4.1-4.2 (m, 1H), 5.4-5.5 (m, 1H), 7.1-7.4 (m, 5H); MS m/e 308 ($M^+ + 1$).

8 b': $^1\text{H NMR } \delta$ 0.86 (t, 3H, J=7 Hz), 1.2-1.7 (m, 14H), 1.83 (s, 3H), 3.1-3.2 (m, 1H), 3.4-3.5 (m, 1H), 5.8-5.9 (m, 1H), 7.1-7.4 (m, 5H); MS m/e 308 ($M^+ + 1$).

8 c: $^1\text{H NMR } \delta$ 1.0-1.5 (m, 4H), 1.6-1.8 (m, 2H), 1.9-2.1 (m, 2H), 3.71 (dq, 1H, J=4, 11 Hz), 4.65 (dt, 1H, J=4, 11 Hz), 5.04 (d, 1H, J=12 Hz), 5.19 (d, 1H, J=12 Hz), 6.7-6.9 (m, 1H), 7.0-7.8 (m, 10H); MS m/e 342 ($M^+ + 1$).

8 c': $^1\text{H NMR } \delta$ 1.1-1.6 (m, 4H), 1.6-1.8 (m, 2H), 2.0-2.4 (m, 2H), 2.90 (dt, 1H, J=4, 10 Hz), 4.65 (dt, 1H, J=4, 10 Hz), 4.8-5.0 (m, 1H), 5.10 (s, 2H), 7.3-7.5 (m, 10H); MS m/e 342 ($M^+ + 1$).

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