Synthesis of 2-(Trimethylsilyl)ethyl Benzenesulfenate and Benzeneselenenate and Their Reaction with Some Electrophiles in the Presence of Tetrabutylammonium Fluoride

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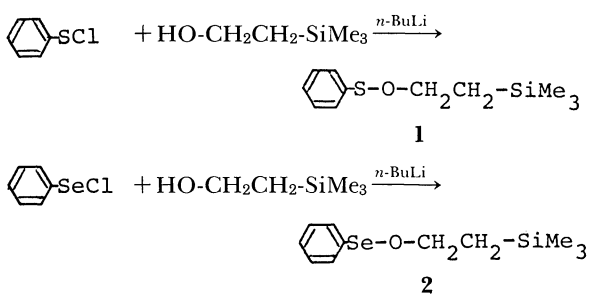
Synopsis. 2-(Trimethylsilyl)ethyl benzenesulfenate was allowed to react with several halides in the presence of tetrabutylammonium fluoride (TBAF) to afford the corresponding phenyl sulfoxides as the main product. In the reaction of 2-(trimethylsilyl)ethyl benzeneselenenate and several halides with TBAF, the corresponding alcohols were obtained as the main product.

When an arenesulfenyl or areneselenenyl halide is allowed to react with an alcohol in order to synthesize the corresponding arenesulfenate or areneselenenate ester, the reaction would rarely be achieved as desired if the halide has no electron-withdrawing group, such as a nitro or keto group on its arene nucleus.[1] Among the arenesulfenate esters[2] isolated previously, only three arenesulfenate esters (methyl benzenesulfenate,[3] methyl and benzyl *p*-toluenesulfenates[4]) were those derived from arenesulfenyl halides having no electron-withdrawing group on their arene nuclei. Also, all of the hitherto isolated areneselenenate esters[5] possess one or two electron-withdrawing groups in their areneselenenic acid moiety. Thus, except methyl alcohol, such alcohol that is capable of converting benzenesulfenyl and/or benzeneselenenyl chlorides, which may be regarded as the parent compounds of arenesulfenyl and/or areneselenenyl halides, to the corresponding benzenesulfenate and/or benzeneselenenate esters has not been found. We propose here 2-(trimethylsilyl)ethyl benzenesulfenate (**1**) and 2-(trimethylsilyl)ethyl benzeneselenenate (**2**) as a new class of arenesulfenate and areneselenenate esters.

The reaction of benzenesulfenyl chloride with 2-(trimethylsilyl)ethanol proceeded by using butyllithium to give **1** in 81% yield after distillation. By the same procedure using benzeneselenenyl chloride instead of benzenesulfenyl chloride, although requiring a relatively lower reaction temperature, **2** was obtained in 56% yield after distillation. The employment of butyllithium in such a condensation reaction has already been reported.[6] It is likely that compound **1** or **2** is structurally a masked benzenesulfenic or benzeneselenenic acid, respectively. Trimethylsilyl 2-nitrobenzenesulfenate[7] is found in the literature as only one example of such a masked sulfenic acid. If the removal of the 2-(trimethylsilyl)ethyl group from **1** or **2** is possible, in analogy with a 2-(trimethylsilyl)ethyl carboxylate,[8] the reaction of the generated benzenesulfenate or benzeneselenenate ion with an appropriate electrophile is expected to occur. Thus, the reactions of **1** or of **2** with some electrophiles in the presence of TBAF were investigated.



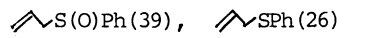
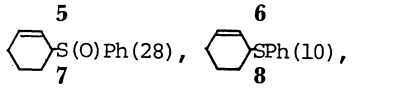
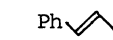
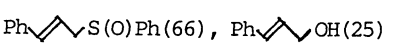
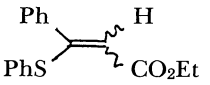
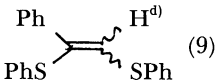
1

2

When a mixture of **1** and any one of alkyl iodides, alkyl bromides, and allyl bromides was allowed to react with TBAF according to Procedure A, the reaction proceeded at room temperature to provide the compounds listed in Table 1. In these cases, except for Run 2 [only in this case, tris(dimethylamino)sulfonium (trimethylsilyl)difluoride was used instead of TBAF], TBAF was used as the fluoride ion source. As can be seen from Table 1, the reaction of **1**, TBAF and an alkyl iodide provided the corresponding alkyl phenyl sulfoxide as the main product. This was also the same as in the reaction of **1**, TBAF and benzyl bromide or an allyl bromide. The reaction seems to proceed via a process involving an initial attack of the fluoride ion and a subsequent elimination of the trimethylsilyl group and the ethylene molecule, leading to a benzenesulfenate ion which is trapped by the electrophile. The removal of the 2-(trimethylsilyl)-ethyl group by a fluoride ion is well-known, although it concerns only the 2-(trimethylsilyl)ethyl carboxylates.[9,10] Probably, **1** is decomposed in a similar manner to the carboxylates by a fluoride ion generated from TBAF. Also, the experimental fact that the yield of alkyl phenyl sulfoxide obtained in the reaction using an alkyl iodide decreases with increasing its molecular weight is consistent with the proposed mechanism. When a solution of **1** (0.113 g, 0.5 mmol) in tetrahydrofuran (THF) (2.5 ml) was mixed initially with a 1.0 M solution (1.5 ml, 1.5 mmol, M=mol dm^{-3}) of TBAF in anhydrous THF and (after stirring for 30 min) methyl iodide (0.036 g, 2.5 mmol) was added followed by stirring for 2 h, methyl phenyl sulfide, butyl phenyl sulfide, diphenyl disulfide(**3**), and methyl phenyl sulfone(**4**) were obtained in 10, 12, 18, and 31% yields, respectively. It is likely that the reaction of the intermediate benzenesulfenate ion with **1**, itself, providing unstable[11] *S*-phenyl benzenethiosulfinate occurred in competition with the reaction of the sulfenate ion with methyl iodide. The thiosulfinate is probably converted to **3**.[11] However, the process by which **4** has been produced remains equivocal.

When a mixture of **1** and an acetylenic compound having one or two electron-withdrawing groups was

Table 1. Reaction of **1** with a Halide or with an Acetylenic Compound in the Presence of TBAF

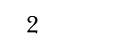
Run	Halide or acetylenic compound	Procedure	Reaction time h	Isolated products[a] (Yield/%)[b]
1	MeI	A	2	PhS(O)Me(66), PhSMe(3), PhS-*n*-Bu(16)
2[c]	MeI	A	11	PhS(O)Me(59), PhSMe(7)
3	EtI	A	6	PhS(O)Et(38), PhSEt(5), PhS-*n*-Bu(15)
4	*n*-PrI	A	2	PhS(O)-*n*-Pr(26), PhS-*n*-Pr(5), PhS-*n*-Bu(15)
5	*n*-BuI	A	24	PhS(O)-*n*-Bu(21), PhS-*n*-Bu(18)
6	$PhCH_2Br$	A	4	$PhS(O)CH_2Ph$(54), $PhSCH_2Ph$(8)
7		A	4	 **5** **6**
8		A	4	 **7** **8** **9**
9		A	4	 **10**
10	$PhC{\equiv}CCO_2Et$	B	4	 (28) **11**
11	$EtO_2CC{\equiv}CCO_2Et$	B	4	$PhSC{\equiv}CCO_2Et$ (67) **12**
12	$PhC{\equiv}CH$	B	4	$PhC{\equiv}C$-SPh (62), **13**  (9) **14**

a) The products **5**—**14** were confirmed by their spectral and analytical data. The sulfides among the other products were confirmed by direct comparison with the commercially available samples. And, the sulfoxides among the other products were comfirmed by direct comparison with the authentic samples prepared by the known method.[13] The compound **13** was also confirmed by direct comparison with the authentic sample prepared by the known method.[14] b) Isolated yield by column chromatography on silica gel using ethyl acetate as eluent. c) Only in Run 2, tris(dimethylamino)sulfonium (trimethylsilyl)difluoride was used instead of TBAF. d) Compound **14** showed the presence of two components on GLC analyses. Further, it was estimated to be a mixture of cis- and trans-isomer with the help of its mass and ^1H NMR spectra.

allowed to react with TBAF according to Procedure B, the reaction proceeded at room temperature or −78 °C to provide the compounds listed also in Table 1. If TBAF was omitted from the reaction system, almost all of the starting substrates were recovered, suggesting the participation of TBAF in these reactions. As can be seen from Table 1, the obtained products varied, depending upon the acetylenic compounds used. Also, the reaction using phenylacetylene provided α,β-bis(phenylthio)styrene (**14**), although it is not the main product. In a somewhat analogous reaction[7] of trimethylsilyl 2-nitrobenzenesulfenate with methyl propynoate, the 2-nitrobenzenesulfinyl moiety of the former had been introduced to the latter. Under our conditions, however, the products obtained were such compounds that the benzenethio moiety of **1** was introduced to the acetylenic compounds used.

When a mixture of **2** and one of benzyl bromide, cinnamyl bromide, 1-chloro-, 1-bromo-, and 1-iodododecane was allowed to react with TBAF according to Procedure C, the reaction proceeded at room temperature to provide the compounds listed in Table 2. As can be seen from Table 2, the obtained products were alcohols which correspond to the halides employed as the trapping agent. Also, in Runs 3—5, a small amount of 1-fluorododecane (**16**) was isolated as a by-product. It is likely that the benzeneselenenate ion formed from **2** and TBAF attacks the halide providing benzeneselenenate ester which is hydrolyzed to the corresponding alcohol together with unstable benzeneselenenic acid. It is likely that the intermediate benzeneselenenate ion attacks a halide used with its oxygen atom. If the ion attacks the halide with its selenium atom, the corresponding phenyl selenoxide would be formed as an intermediate. For example, in Run 1, benzyl phenyl selenoxide would be formed and isolated without any further alteration due to its invariability. However, none of benzyl phenyl selenoxide was obtained in Run 1. This suggests that the benzeneselenenate ion has a pair of available electrons only on its oxygen atom as a nucleophile. In a separate experiment, a solution containing benzyl phenyl selenoxide[12] (0.13 g, 0.5 mmol), a 1.0 M solution (1.0 ml, 1.0 mmol) of TBAF in anhydrous THF and tetrabutylammonium bromide (0.16 g, 0.5 mmol) in THF (2.5 ml) was stirred at room temperature for 7 h. The forma-

Table 2. Reaction of **2** with a Halide in the Presence of TBAF

Run	Halide	Procedure	Reaction time (h)	Isolated product[a] (Yield/%)[b]
1	$PhCH_2Br$	C	7	$PhCH_2OH$ (100)
2		C	7	 (65)
3	$Me(CH_2)_{11}Cl$	C	48	$Me(CH_2)_{11}OH$ (19), $Me(CH_2)_{11}F$(2), **15** **16** $Me(CH_2)_{11}Cl$[c] (36)
4	$Me(CH_2)_{11}Br$	C	7	**15**(43), **16**(2), $Me(CH_2)_9CH{=}CH_2$(trace)
5	$Me(CH_2)_{11}I$	C	7	**15**(49), **16**(3)

a) Except **16**, the products in this table were confirmed by direct comparison with the commercially available samples. The compound **16** was confirmed by its spectral and analytical data. b) Yields of alcohols were determined by GLC analysis with 1-tetradecanol as an internal standard. Other yields were obtained by column chromatography on silica gel using hexane or 10% ethyl acetate-hexane as eluent. c) Recovered 1-chlorododecane.

tion of benzyl alcohol, however, could not be recognized after a similar work up as in Procedure C. This experimental fact seems to support the above suggestion.

Experimental

Synthesis of 1. To a stirred, cooled (−78 °C) solution of 2-(trimethylsilyl)ethanol (2.03 g, 17.2 mmol) in ether (110 ml) was added (during 5 min, by syringe under nitrogen) a 1.6 M solution of butyllithium (11.7 ml, 18.7 mmol) in hexane. This mixture was stirred under nitrogen for 30 min at the same temperature and a solution of benzenesulfenyl chloride (2.26 g, 15.6 mmol) in ether (20 ml) was then dropped in. This mixture was allowed to warm to room temperature, stirred for 4 h, filtered, and concentrated in vacuo to give a residue which was distilled, bp, 74—80 °C/2 Torr (1 Torr=133.322 Pa), yield 81%. ^{1}H NMR ($CDCl_3$) δ=0.01 (s, 9H), 1.1—1.2 (m, 2H) , 3.8—3.9 (m, 2H), and 7.1—7.4 (m, 5H).

Synthesis of 2. To a stirred, cooled (−78 °C) solution of 2-(trimethylsilyl)ethanol (1.36 g, 11.5 mmol) in ether (100 ml) was added (during 5 min, by syringe under nitrogen) a 1.6 M solution (7.2 ml, 11.5 mmol) of butyllithium in hexane. The mixture was stirred under nitrogen for 30 min at −78 °C and a solution of benzeneselenenyl chloride (2.20 g, 11.5 mmol) in ether (40 ml) was dropped in. Then, the mixture was stirred for 4 h, during which time it was allowed to slowly warm to −30 °C. The mixture was concentrated in vacuo at −30 °C to give a residue. After adding a large quantity of pentane to the residue, it was filtered and concentrated in vacuo to give the crude product which was distilled, bp 77—83 °C/2 Torr, yield 56%. ^{1}H NMR ($CDCl_3$) δ=0.01 (s, 9H) , 1.0—1.1 (m, 2H), 3.9—4.0 (m, 2H), 7.2—7.5 (m, 3H), and 7.5—7.6 (m, 2H).

Reaction of 1 and a Halide with TBAF (Procedure A). To a stirred solution of **1** (0.113 g, 0.5 mmol) and any one of alkyl iodides (2.5 mmol), alkyl bromides (2.5 mmol), and allyl bromides (1.2 mmol) in THF (2.5 ml) was added, under nitrogen, a 1.0 M solution (1.5 ml, 1.5 mmol) of TBAF in anhydrous THF. The mixture was stirred under nitrogen at room temperature. After adding excess ether to the mixture, it was filtered, and evaporated in vacuo to give a residue which was subjected to column chromatography on silica gel.

Reaction of 1 and an Acetylenic Compound with TBAF (Procedure B). To a cooled (−78 °C), stirred solution of **1** (0.113 g, 0.5 mmol) and an acetylenic compound (1.0 mmol) in THF (2.5 ml) was added, under nitrogen, a 1.0 M solution (1.5 ml, 1.5 mmol) of TBAF in anhydrous THF. The mixture was stirred under nitrogen for 4 h at −78 °C (Run 11) or at room temperature (Runs 10 and 12) after being allowed to warm to that temperature, and worked up in a similar manner as mentioned above.

Reaction of 2 and a Halide with TBAF (Procedure C). To a stirred solution of **2** (0.156 g, 0.55 mmol) in THF (2.5 ml) was added successively, under nitrogen, a halide (0.77 mmol) and a 1.0 M solution (1.65 ml,1.65 mmol) of TBAF in anhydrous THF. The mixture was stirred under nitrogen at room temperature. After adding excess ether to the mixture, it was filtered, washed with water, dried over Na_2SO_4, and evaporated in vacuo to give a residue which was subjected to column chromatography on silica gel.

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