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Oxidative Arylation Mediated by Naphthalene-1,8-diylbis(diphenylmethylium): Synthetic Route to Triarylsulfonium Salts

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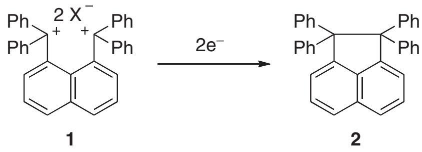
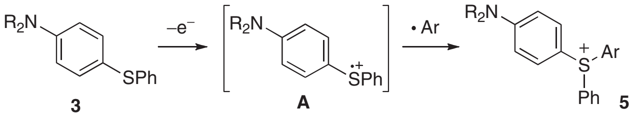
Dicationic species, naphthalene-1,8-diylbis(diphenylmethylium), successfully promoted oxidative arylation of the sulfur atom in (4-*N*,*N*-dialkylaminophenyl) phenyl sulfides with (4-*N*,*N*-dialkylaminopheny)silanes, affording triarylsulfonium salts in good yield.

Triarylsulfonium salts are highly sensitive to photolytic C–S bond cleavage, which causes an efficient proton generation.[1] This process allows triarylsulfonium salts to be well utilized as an efficient photochemical source of Brønsted acids in industrial processes such as cationic polymerization of alkenes or oxiranes and hydrolysis in photoresist technology.[2,3] In view of the practical role of these salts, synthetic methods to produce them are still needed. Although a number of synthetic methods for alkylsulfonium salts have been described in the literature,[4] there are few methods on the synthesis of triarylsulfonium salts, and fewer methods starting from diaryl sulfides. Triarylsulfonium salts are synthesized by the reaction of diaryl sulfoxides with aryl Grignard reagents and silylating reagents,[5] but there is the drawback that excess amounts of both reagents are required. Diaryliodonium salts[6] and aryl formates[7] are used for the synthesis of triarylsulfonium salts directly from diaryl sulfides, albeit in low yield. Thus, triarylsulfonium salt synthesis by direct arylation of sulfides still remains to be developed.

Recently, we found that naphthalene-1,8-diylbis(diphenylmethylium) (**1**) acts as an efficient, organic two-electron oxidant.[8,9] The dication **1** readily undergoes reduction via electron transfer with an especially high oxidation potential, compared with those of other bis(triarylmethylium)s[10] and monotriarylmethyliums.[11] In this process, a neutral compound, 1,1,2,2-tetraphenylacenaphthene (**2**), is formed via C–C bond formation between the two carbocationic centers (Scheme 1). Syntheses of (i) benzidines via self-coupling of *N*,*N*-dialkylanilines[8a] and (ii) diaryl ethers via arylation of phenols with (4-*N*,*N*-dialkylaminophenyl) phenyl sulfides[8b] have already been accomplished using dication **1**. In the latter case, diaryl sulfides **3** are oxidized to generate stable radical cation species **A**.[12] We envisaged that radical cations **A** might be captured by an aryl radical equivalent, providing an entry to triarylsulfonium salts **5** directly from diaryl sulfides (Scheme 2). In this communication, we report an oxidative method using dication **1** for the synthesis of triarylsulfonium salts via arylation of diaryl sulfides with arylsilanes.[13]

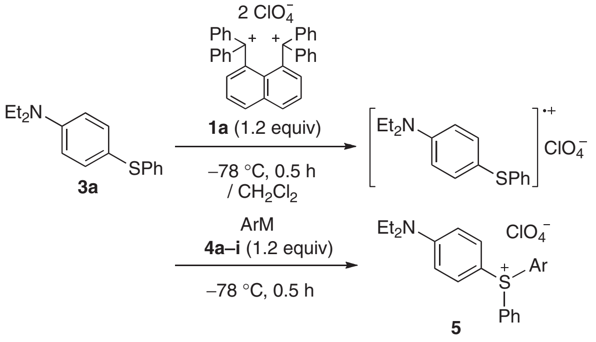


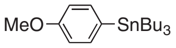
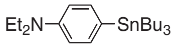
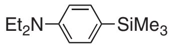
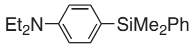
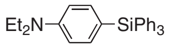
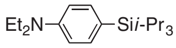
Scheme 1. Two-electron transfer to dication **1**.



Scheme 2. Triarylsulfonium salt synthesis via oxidative arylation of sulfides.

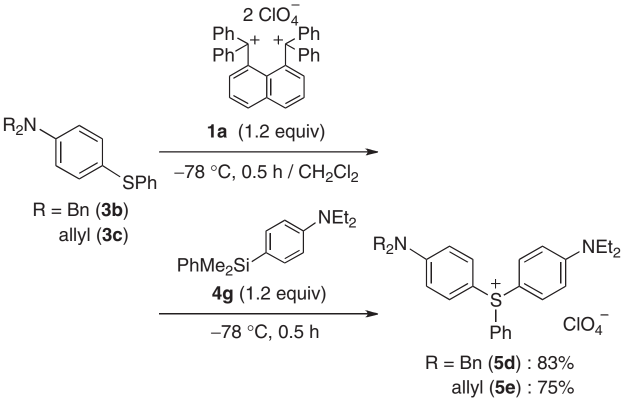
Table 1. Oxidative arylation of sulfide **3a** with arylmetals **4a**–**4i**



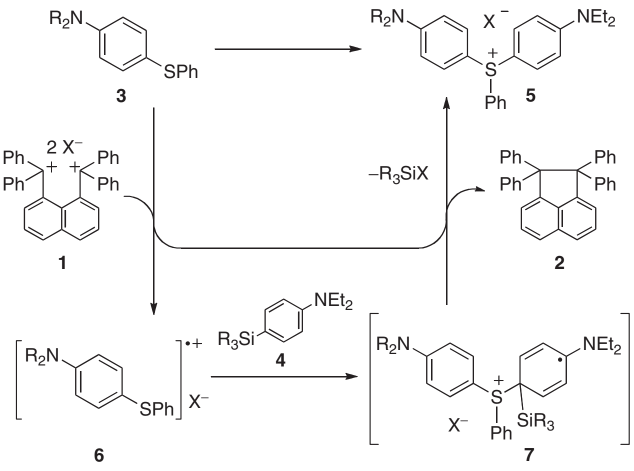
Entry	ArM		Yield/%
1	PhLi	(**4a**)	<15 (**5a**)
2	PhMgBr	(**4b**)	< 7 (**5a**)
3	PhSnBu$_3$	(**4c**)	0
4		(**4d**)	0
5		(**4e**)	88 (**5b**)
6		(**4f**)	77 (**5b**)
7 8		(**4g**)	80 (**5b**) 73[a] (**5c**)
9		(**4h**)	46 (**5b**)
10		(**4i**)	<12 (**5b**)

[a]Using dication **1b** (X = OTf) as an oxidant gave triflate salt **5c**.

First, we screened several aryl metal species that we expected to act as aryl radical sources under oxidative conditions. Diaryl sulfide **3a** was successively treated with dication **1a** (X = ClO_4) and **4a**–**4i** at −78 °C in dichloromethane. The results are summarized in Table 1. Phenyllithium and phenylmagnesium reagents **4a** and **4b** afforded triarylsulfonium salt **5a** in low yield, along with biphenyl as a major product (Entries 1 and 2). Phenyl- and 4-methoxyphenylstannanes **4c** and **4d** failed to produce sulfonium salts, but 4-diethylaminophenylstannane **4e** gave the expected sulfonium



Scheme 3. Oxidative arylation of sulfides **3b** and **3c**.



Scheme 4. A plausible mechanism for oxidative arylation on sulfur.

salt **5b** in 88% yield (Entry 5), along with 83% yield of **2**, which can be recycled.[8a] Moreover, (4-diethylaminophenyl)trimethylsilane (**4f**) showed similar reactivity. Subsequently, we investigated several aminophenylsilanes. (4-Diethylaminophenyl)dimethylphenylsilane (**4g**) reacted with sulfide **3a** to give **5b** in 80% yield (Entry 7),[14,15] while the yields were low in the cases of the corresponding triphenylsilane **4h** and triisopropylsilane **4i** (Entries 9 and 10). In addition, triflate salt **1b** (X = OTf) was also effective as an oxidant for arylation of sulfide **3a** to give triarylsulfonium triflate **5c** in 73% yield (Entry 8). Other oxidizing agents, such as CAN, $(p\text{-BrC}_6\text{H}_4)_3\text{N}^{+\bullet}[\text{SbCl}_6]^-$, DDQ, and PhI(OAc)$_2$, gave poor results (0%,[16] 26%, trace, and 0% yield, respectively) in this triarylsulfonium salt synthesis with **4g**.

To explore the scope of oxidative triarylsulfonium formation, we surveyed the effect of substituents on the nitrogen atom of sulfides **3**, such as benzyl and allyl groups, which can be deprotected under reductive conditions. As shown in Scheme 3, **3b** and **3c** provided **5d** and **5e** in 83% and 75% yield, respectively. Deprotection of groups on the nitrogen provides an amino group, which acts as a surrogate for a wide range of functional groups.

A plausible reaction mechanism for the above-mentioned arylation of sulfides is shown in Scheme 4. Treatment of diaryl sulfides **3** with dication **1** generates stable radical cations **6**, which are trapped by silanes **4** on the sulfur atom to give sulfonium radical cations **7**.[12] Further oxidation of **7** and elimination of the silyl group occurs successively to afford triarylsulfonium salts **5**.[17]

In conclusion, triarylsulfonium salts were readily synthesized in good yield from (4-*N*,*N*-dialkylaminophenyl) phenyl sulfides and (4-*N*,*N*-diethylaminophenyl)silanes. This oxidative arylation of sulfides was successfully promoted by dication **1** via two-electron oxidation. Because there are few methods for the synthesis of triarylsulfonium salts, such direct arylation of diarylsulfides provides a promising access to triarylsulfonium salts.

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12 The SOMO of the radical cation **A** (R = Et) has the largest coefficient on the sulfur atom. See Ref. 8b.

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14 To a solution of **3a** (26 mg, 0.10 mmol) in CH$_2$Cl$_2$ (2.0 mL) was added **1a** (80 mg, 0.12 mmol) at −78 °C. After the reaction mixture was stirred for 0.5 h at −78 °C, **4g** (35 mg, 0.12 mmol) was added. After stirring for 0.5 h at −78 °C, the reaction was quenched with saturated aq NaHCO$_3$ and the aqueous layer was extracted with CH$_2$Cl$_2$. The combined extracts were washed with brine and dried over Na$_2$SO$_4$. After removal of the solvent, the residue was purified by preparative TLC to afford **5b** (40 mg, 80%) as pale yellow crystals.

15 When **3a** was added to the mixture of **4g** and **1a**, **5b** was obtained in 64% yield.

16 The reaction was conducted in DMF at room temperature for 1 h.

17 There is another possible pathway from radical cations **6** to sulfonium salts **5**. Arylsilanes **4** could be oxidized by dication **1** to generate the corresponding aryl radicals, which would react with **6** to give **5**. However, we failed to trap the aryl radicals.