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

Hiroyuki Tanabe,1 Takaharu Kawai,2 Terunobu Saitoh,2 and Junji Ichikawa*1

1Department of Chemistry, Graduate School of Pure and Applied Sciences, University of Tsukuba, Tsukuba 305-8571
2Department of Chemistry, Graduate School of Science, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113-0033

(Received October 15, 2009; CL-090929; E-mail: junji@chem.tsukuba.ac.jp)

Two-Electron Oxidation

Reprinted from Chemistry Letters
Vol. 39 No. 1 2010 p.56–57
The Chemical Society of Japan

Published on the web December 12, 2009; doi:10.1246/cl.2010.56
Dicatonic species, naphthalene-1,8-diylbis(diphenylmethylium), successfully promoted oxidative arylation of the sulfur atom in (4-η,η-dialkylaminophenyl) phenyl sulfides with (4-η,η-dialkylaminophenyl)silanes, affording triarylsulfonium salts in good yield.

Triarylsulfonium salts are highly sensitive to photolytic C–S bond cleavage, which causes an efficient proton generation. 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 alkynes or oxiranes and hydrolysis in photoresist technology. 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, 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, but there is the drawback that excess amounts of both reagents are required. Diaryiodonium salts and aryl formates 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. The dication 1 readily undergoes reduction via electron transfer with an especially high oxidation potential, compared with those of other bis(aryl)methylum salts and monoirylmethylum. 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 and (ii) diaryl ethers via arylation of phenols with (4-η,η-dialkylaminophenyl) phenyl sulfides 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 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.

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 = ClO4) 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 1. Two-electron transfer to dication 1.](image1)

![Scheme 2. Triarylsulfonium salt synthesis via oxidative arylation of sulfides.](image2)

<table>
<thead>
<tr>
<th>Entry</th>
<th>ArM</th>
<th>Yield%</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>PhLi</td>
<td>4a</td>
</tr>
<tr>
<td>2</td>
<td>PhMeBr</td>
<td>4b</td>
</tr>
<tr>
<td>3</td>
<td>PhSnBu3</td>
<td>4c</td>
</tr>
<tr>
<td>4</td>
<td>MeO−</td>
<td>PhSnBu3</td>
</tr>
<tr>
<td>5</td>
<td>El2N−</td>
<td>SnBu3</td>
</tr>
<tr>
<td>6</td>
<td>El2N−</td>
<td>SiMe3</td>
</tr>
<tr>
<td>7</td>
<td>El2N−</td>
<td>SiMe3</td>
</tr>
<tr>
<td>8</td>
<td>El2N−</td>
<td>SiPh3</td>
</tr>
<tr>
<td>9</td>
<td>El2N−</td>
<td>Si-Pr3</td>
</tr>
<tr>
<td>10</td>
<td>El2N−</td>
<td>Si-Pr3</td>
</tr>
</tbody>
</table>

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

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

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

In conclusion, triarylsulfonium salts were readily synthesized in good yield from (4-N,N-dialkylaminophenyl) phenyl sulfides and (4-N,N-diethy lam inophenyl) silanes. This oxidative arylation of sulfides was successfully promoted by dicaticn 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.

References and Notes
12. The SOROM of the radical cation (R = Et) has the largest coefficient on the sulfur atom. See Ref. 8b.
14. To a solution of 3a (26 mg, 0.10 mmol) in CH2Cl2 (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 Na2CO3 and the aqueous layer was extracted with CH2Cl2. The combined extracts were washed with brine and dried over Na2SO4. 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 dicaticn 1 to generate the corresponding aryl radicals, which would react with 6 to give 5. However, we failed to trap the aryl radicals.