A Platinum Open Access Journal
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Paper

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DOAJ Seal

Arkivoc **2021**, part vii, 0-0
to be inserted by editorial office

Catalytic and non-catalytic selective aryl transfer from (mesityl)iodonium(III) salts to diarylsulfide compounds

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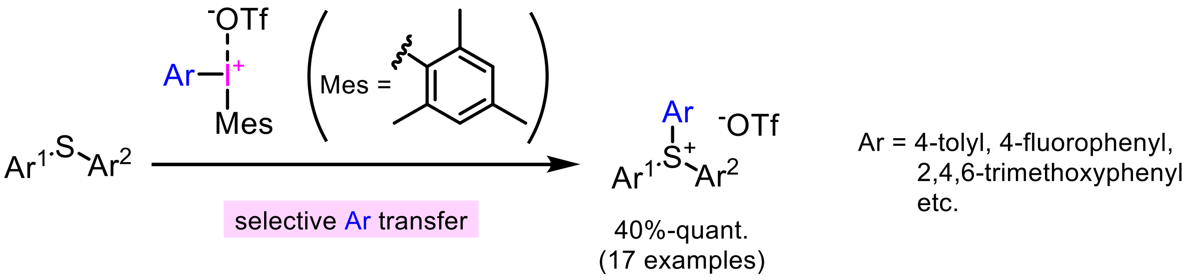
Received 01-28-2022 **Accepted Manuscript** 03-18-2022 **Published on line** 04-11-2022

Abstract

We report a facile synthesis of triarylsulfonium triflates by selective aryl transfer from readily available mesityl iodonium(III) salts to diarylsulfides in the presence of a copper catalyst. The advantage of our protocol is that the iodonium(III) salts bearing a mesitylene (Mes) auxiliary efficiently promote selective *S*-arylation of diarylsulfides to produce the desired triarylsulfonium triflates without the formation of Mes-derived byproduct salts.

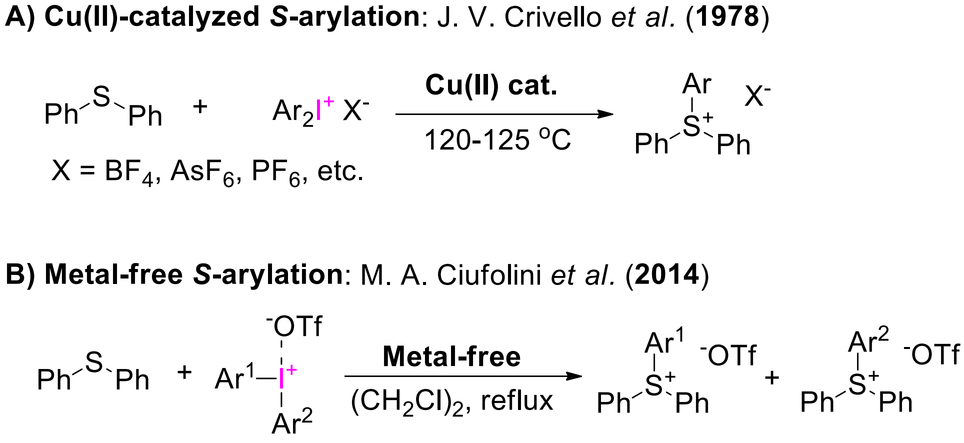


Keywords: Hypervalent compounds, iodine, diaryliodonium(III) salts, ligand transfer selectivity, sulfonium salts

DOI: https://doi.org/10.24820/ark.5550190.p011.732

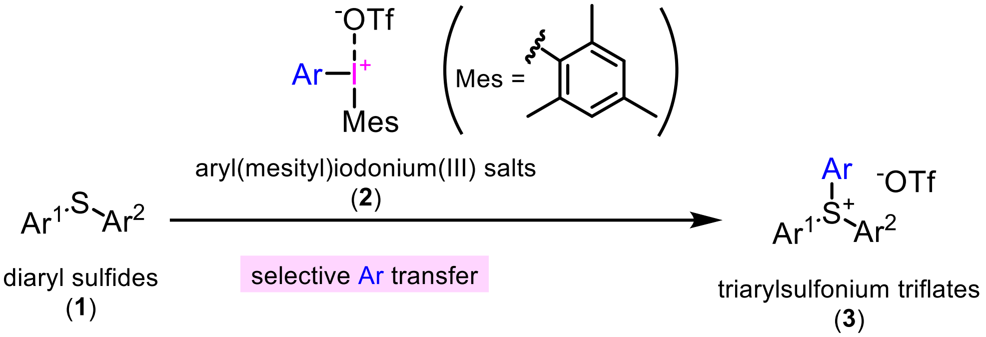
Introduction

Triarylsulfonium salts, one of the useful and important classes of sulfonium salts from an industrial point of view, have a wide range of applications, e.g., as acid generators in photolithography or as photoinitiators in cationic polymerization.[1,2] Recently, triarylsulfonium salts have received considerable attention in organic synthesis as radical precursors and cross-coupling partners in metal-catalysis.[3] Several synthetic routes for preparing triarylsulfonium salts have thus been reported so far.[4] Among them, aryl transfer from diaryliodonium(III) salts to diarylsulfides under simple operation is one of the most reliable approaches.[5-8] In early studies, around 1960s, non-catalytic arylation of Ph_2S with $Ph_2I^+BF_4^-$ under harsh conditions (180 °C, 35 h) was reported to afford $Ph_3S^+BF_4^-$ in a moderate yield (ca. 65%).[5] In 1978, Crivello *et al.* reported a faster and better-yield aryl transfer reaction in the presence of catalytic $Cu(OBz)_2$ (Scheme 1A),[6] but the reaction used a limited number of diaryliodonium(III) salts ($Ar^1Ar^2I^+X^−$; $Ar^1 = Ar^2$) possessing non-nucleophilic counter anions such as BF_4^-, AsF_6^-, and PF_6^-. In 2014, Ciufolini *et al.* demonstrated that diaryliodonium(III) triflates effectively arylate diarylsulfide compounds under transition-metal-free conditions (Scheme 1B).[7] The synthetic method is an attractive and economically advantageous approach, but mixtures of two types of aryl-transferred triarylsulfonium triflates were obtained in the case of diaryliodonium(III) triflates having $Ar^1 \neq Ar^2$. Thus, developing a more practical method that enables the use of various diaryliodonium(III) salts is still required to expand the synthetic scope for triarylsulfonium salts with greater structural diversities.



Scheme 1. *S*-Arylation of diarylsulfides with diaryliodonium(III) salts.

Diaryliodonium(III) salts have found numerous applications as electrophilic arylating agents toward nucleophiles, and the nature of the aryl moiety and anionic counterpart alter their chemical and physical properties.[9-11] Over the past few decades, diaryliodonium(III) salts ($Ar^1Ar^2I^+X^−$) with $Ar^1 = Ar^2$ were preferred over those with $Ar^1 \neq Ar^2$ in order to avoid selectivity issues of aryl transfer processes. Recently, aiming at selective aryl transfer reactions, specific diaryliodonium(III) salts incorporating a non-transferable dummy group such as mesityl (Mes)[12-14] and an auxiliary 2,4,6-trimethoxyphenyl (TMP)[15-19] have been studied by scientists including our research group. In our continuous study of diaryliodonium(III) salts-mediated reactions,[20,21] we report herein diaryliodonium(III) triflates bearing a mesitylene (Mes) auxiliary to facilitate selective *S*-arylation of diarylsulfides to form triarylsulfonium triflates without the formation of Mes-derived byproduct salts (Scheme 2).

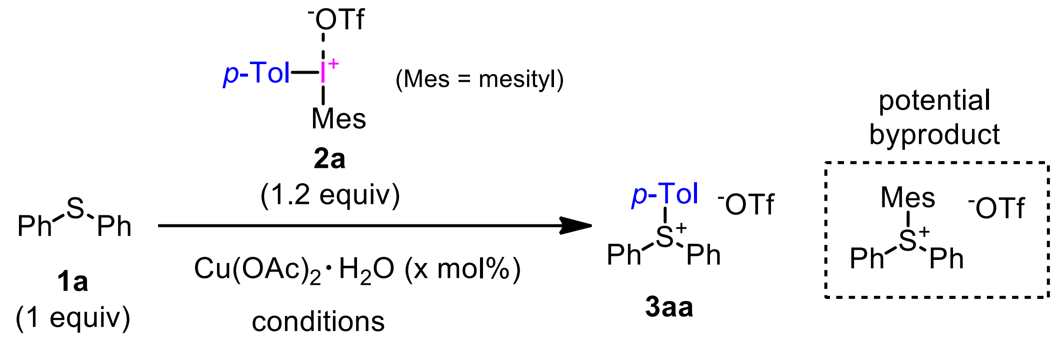


Scheme 2. This work : selective *S*-arylation of diarylsulfides with (mesityl)iodonium(III) triflates.

Results and Discussion

In a pilot experiment, we first examined the *S*-arylation of diphenylsulfide **1a** in the presence of copper(II) acetate monohydrate[22] using mesityl(*p*-tolyl)iodonium(III) triflate **2a** (Table 1). When sulfide **1a** was reacted with 1.2 equivalent of iodonium(III) triflate **2a** with 10 mol % of copper(II) acetate monohydrate at 130 °C under solvent-free conditions, the reaction proceeded smoothly and yielded the arylation product **3aa** with an 80% and 91% yields (Entries 1 and 2, respectively). It is notable that the sulfonium salt **3aa** was solely obtained by selective *p*-tolyl transfer in high yields without the formation of a potential byproduct, diphenyl(mesityl)sulfonium salt. The copper(II)-catalyzed aryl transfer of (mesityl)iodonium(III) salts was reported in other arylation reactions, in which the oxidative addition of copper(II) to the mesityl group did not occur due to its high steric bulkiness. The use of 1,2-dichloroethane (DCE) as solvent also resulted in a good yield with selective formation of **3aa**, though the reaction time in this case was prolonged (Entries 3 and 4). Lowering the reaction temperature to 100 °C increased the yield to 96% (Entries 5 and 6). The usage of anhydrous copper(II) acetate was not effective, and provided an inferior result in comparison with the use of copper(II) acetate monohydrate (Entry 7). Moreover, when the reaction was performed with equimolar amounts of diphenylsulfide **1a** and iodonium(III) triflate **2a**, the yield was slightly decreased (Entry 8). It should be noted that the copper(II) catalyst plays an important role in accelerating the reaction rate; the use of 5 mol % of copper(II) gave *p*-tolyl transfer product **3aa** with an 88% yield at 100 °C (Entry 9), while the same product was not obtained at all in the absence of the copper(II) catalyst (Entry 10).

Table 1. Optimization of the reaction conditions

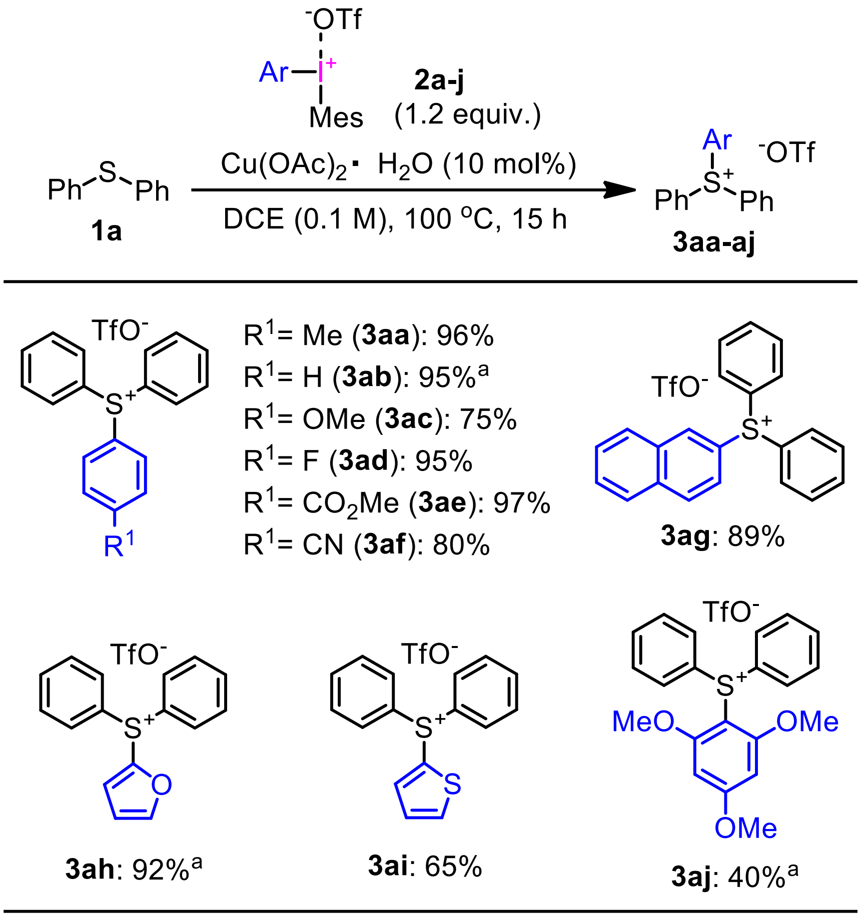


Entry	X	Temp	Solvent[a]	Time	Yield[b]
1	10	130 °C	none	30 min	80%
2	10	130 °C	none	2 h	91%
3	10	130 °C	DCE	2 h	79%
4	10	130 °C	DCE	15 h	77%
5	10	100 °C	DCE	2 h	89%
6	10	100 °C	DCE	15 h	96%
7[c]	10	100 °C	DCE	15 h	89%
8[d]	10	100 °C	DCE	15 h	80%
9	5	100 °C	DCE	15 h	88%
10	none	100 °C	DCE	15 h	nd

a: **1a** (0.1 M); b: isolate yield of sulfonium salt **3aa**; c: Cu(OAc)$_2$ was used; d: equimolar amounts of **1a** and **2a** were used.

With the optimal reaction conditions identified (Table 1, entry 6), we explored the reaction scope of iodonium(III) triflates **2** for diphenylsulfide **1a**. As shown in Table 2, diverse aryl(mesityl)iodonium(III) triflates **2** were found to undergo the desired sulfonium salt formation. Mesityl(phenyl)iodonium(III) triflate **2b** and triflate **2c** bearing an electron-donating methoxy group, as well as triflates **2d**-**f** bearing electron-withdrawing groups, all produced the expected sulfonium salts **3ab**-**3af** with yields of 75-97%, though a higher reaction temperature (130 °C) was necessary for improving the yields in some cases. The reaction of sulfide **1a** and mesityl(naphthyl)iodonium(III) triflates **2g** also proceeded to afford the corresponding product **3ag** with a yield of 89%. When triflates **2h** and **2i** containing heteroaromatics, such as furan and thiophene, were subjected to the reaction conditions, the desired heteroaryl sulfonium salts **3ah** and **3ai** were also obtained with a 92% and 65% yield, respectively. The aryl transfer reaction of triflate **2j** bearing a sterically bulky 2,4,6-trimethoxyphenyl (TMP) group did not smoothly proceed at 100 °C, while the corresponding product **3aj** was obtained with a moderate yield (40%) when the temperature was increased to 130 °C. Note that all the sulfonium products **3aa**-**3aj** were selectively obtained in good yields without the formation of potential byproducts, Mes-derived sulfonium salts.

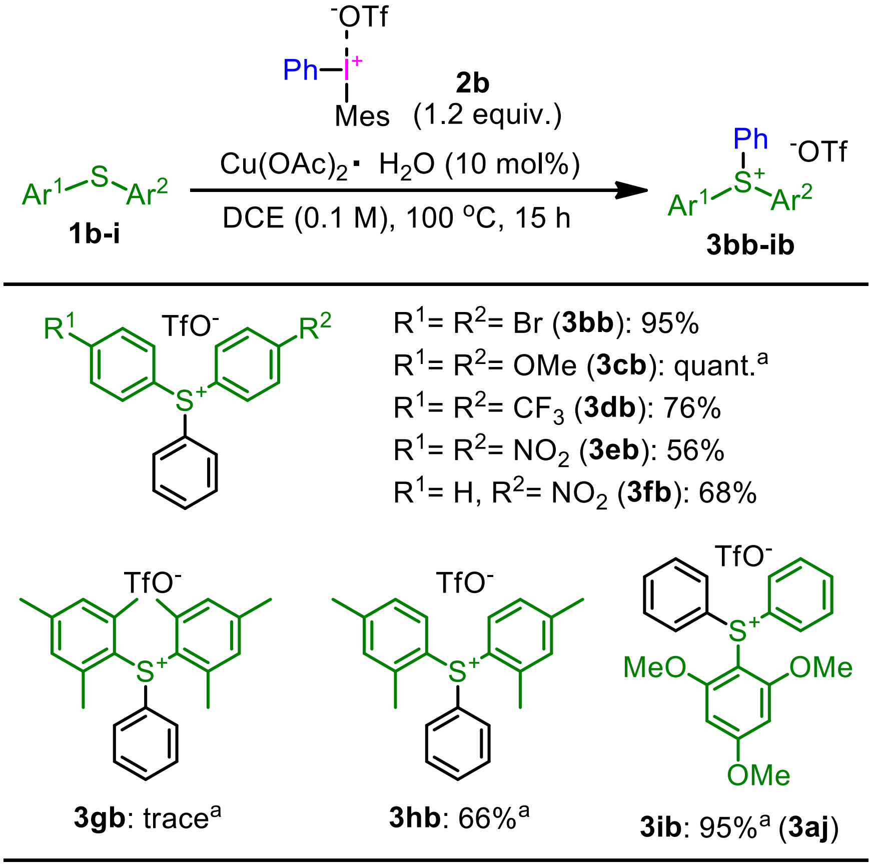
Table 2. Scope of aryl(mesityl)iodonium(III) salts **2**



a: Reactions were performed at 130 °C.

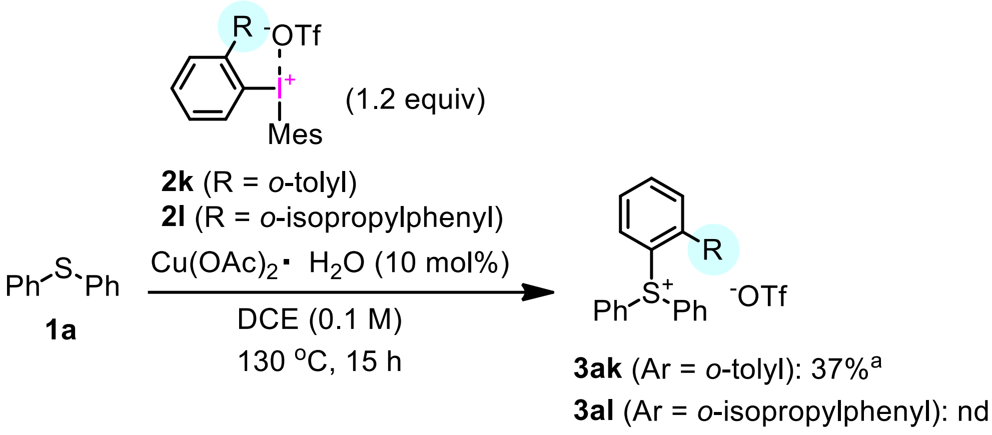
As summarized in Table 3, the generality of the aryl-transfer protocol using mesityl(phenyl)iodonium(III) triflate **2b** for various diarylsulfides **1b**-**1i** was also investigated under the optimized reaction conditions. Irrespective of the presence of the electron-donating or electron-withdrawing groups on the aromatic rings, diarylsulfides **1b**-**1e** were capable of forming sulfonium salts **3bb**-**3eb** in good to excellent yields. However, it was necessary to increase the temperature for accelerating the reaction of electron-rich diarylsulfide **1c**. Arylation of *p*-nitrophenyl(phenyl)sulfide **1f** also proceeded to afford the resulting product **3fb** with a 68% yield. As for sterically hindered and electron-rich diarylsulfides **1g**-**1i**, the reactions did not proceed smoothly at 100 °C. The corresponding sulfonium salts **3hb** and **3ib** could be obtained at 130 °C with yields of 66% and 95%, respectively, but the reaction of diarylsulfide **2g** bearing a sterically bulky and electron-rich mesityl group did not proceed even at an elevated temperature. Compared to the iodonium(III) salt scope, the *ortho*-aromatic substituents in diarylsulfides had little influence on the reaction progress (see the formations of diphenyl(2,4,6-trimethoxyphenyl)sulfonium triflate **3aj** in Table 2 and **3ib** in Table 3).

Table 3. Scope of diarylsulfides **1** coupled with mesityl(phenyl)iodonium(III) triflate **2b**



a: Reactions were performed at 130 °C.

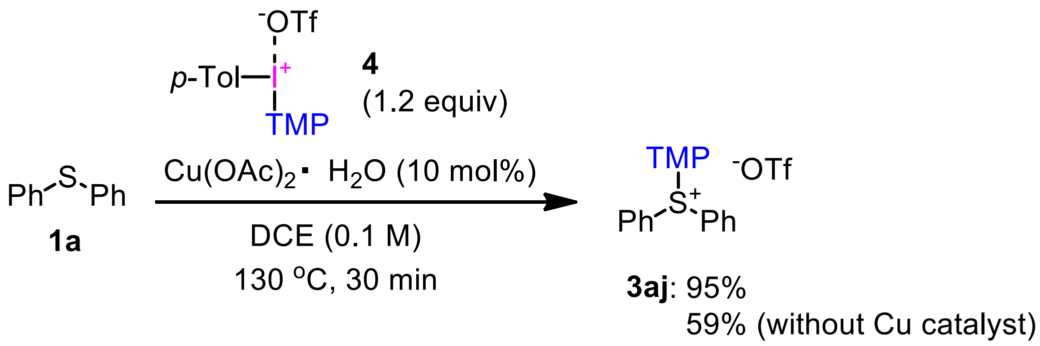
It seems that the steric effect of the iodonium(III) mesityl group is the origin of the selective aryl transfer in this sulfonium salt formation. This is evident from the slow transfer of *o*-tolyl group from (mesityl)iodonium(III) triflate **2k** to diphenylsulfide **1a** with only a 37% formation of the corresponding sulfonium salt **3ak**, while mesityl group was not transferred under the reaction conditions (Scheme 3). Furthermore, the reaction of iodonium(III) triflate **2l** bearing a sterically bulky *o*-isopropylphenyl group did not proceed, and the sulfonium salt **3al** was not obtained at all. This is the limitation of scope of the developed protocol, where the iodonium(III) salts **2** bearing *ortho*-substituents prevent the aryl transfer reaction. On the other hand, reaction of (*o*-isopropylphenyl)(*p*-tolyl)iodonium(III) triflate with diphenylsulfide **1a** by the same copper catalysis selectively afforded *p*-tolyl transfer product, diphenyl(*p*-tolyl)sulfonium triflate, in a nearly quantitative yield. Therefore, such sterically hindered *ortho*-substituted aryl group would serve as a dummy ligand in diaryliodonium(III) salts during the present aryl transfer process to diarylsulfide compounds.



[a]: ^{1}H-NMR yield ; nd : not detected.

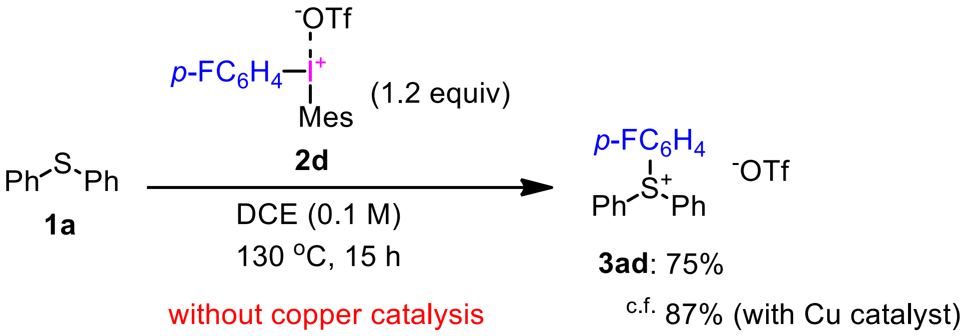
Scheme 3. *ortho*-Group steric effect.

We then examined the reaction of diphenylsulfide **1a** using other specific iodonium(III) triflate **4** with a TMP group, which is used as a non-transferable dummy group in a range of metal-free and metal-catalyzed coupling reactions[15-19] (Scheme 4). The reaction was completed within 30 min under the catalytic conditions. However, the TMP group did not work as a non-transferable aryl group and TMP-transferred sulfonium salt **3aj** was obtained with a 95% yield. In the absence of the copper catalyst, TMP group was similarly transferred to afford the same sulfonium salt **3aj** with a yield of 59%. Therefore, the TMP group is too electron-rich to be suitable for the present *S*-arylation of diarylsulfides **1**, while the Mes group is a suitable auxiliary in iodonium(III) salts for the selective aryl transfer. As such, TMP-iodonium(III) salt **4** showed inherently different aryl transfer reactivity in the present case compared to other reported coupling reactions.[19]



Scheme 4. TMP-group transfer from TMP-iodonium(III) salt **4.**

Finally, a non-catalytic aryl transfer reactivity of mesityliodonium(III) salt was performed, as shown in Scheme 5. The reaction of diphenyl sulfide **1a** and *p*-fluorophenyl(mesityl)iodonium(III) triflate **2d** without the copper catalysis proceeded under the thermal conditions at 130°C to form diphenyl(*p*-fluorophenyl)sulfonium triflate **3ad** with a yield of 75%. Meanwhile, when the reaction was performed using 10 mol % of copper(II) acetate monohydrate at 130 °C, the same sulfonium salt **3ad** was obtained with a yield of 87%. This result implied that the reaction would proceed faster and with a better yield in the presence of the copper catalyst. In contrast, selective aryl transfer occurred without the need of the copper catalyst, which was achieved by utilizing (mesityl)iodonium(III) triflate **2d**. Accordingly, the Mes auxiliary of diaryliodonium(III) salts **2** is crucial for achieving the selective aryl transfer, and yielding single triarylsulfonium salts **3** in the present *S*-arylation of diarylsulfides **1**.



Scheme 5. Non-catalytic selective aryl transfer from (mesityl)iodonium(III) salt **2d.**

Conclusions

We have developed a facile method for the preparation of a variety of triarylsulfonium triflates **3** by selective aryl-group transfer utilizing aryl(mesityl)iodonium(III) salts **2**. It was revealed that the mesityl (Mes) group specifically contributes to the selective *S*-arylation of diarylsulfides **1** to form variety of the desired sulfonium triflates **3**, and in which the *ortho*-steric effect of mesityliodonium(III) salts seems to prevent the formation of Mes-transferred byproducts.

Experimental Section

General. Diarylsulfides (**1d**, **1f**, **1g**, **1h**, and **1i**)[23-26] and mesityliodonium(III) salts **2**[14] were prepared according to the reported methods and our procedure. Other materials were used as received from commercial sources without further purification. Melting points (MPs) were measured using a Büchi B 545 apparatus and are uncorrected. Infrared (IR) spectra were obtained using a Hitachi 270-50 spectrometer; absorptions are reported in reciprocal centimeters (cm^{-1}) for strong and structurally important peaks. ^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectra were recorded on a JEOL JMN-400 spectrometer operating at 400 MHz (^{1}H NMR) in $CDCl_3$ and 100 MHz (^{13}C NMR) in DMSO-*d*$_6$ at 25 °C. The chemical shifts in ^{1}H and ^{13}C NMR spectra were recorded relative to the residual solvent peaks ($CDCl_3$: δ 7.26, DMSO-*d*$_6$: δ 39.5). The date are reported as follows : chemical shift in ppm (δ), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, dd = double-doublet, m = multiplet), coupling constant (Hz), and integration. High-resolution mass spectra (HRMS) were obtained using a Thermo Scientific Exaxtive Plus Orbitrap (Thermo Fisher Scientific, Inc., Waltham, MA, USA). Flash column chromatography and analytical thin layer chromatography (TLC) were carried out on Merck Silica gel 60 (230-400 mesh) and Merck Silica gel F_{254} plates (0.25 mm), respectively. The spots and bands were detected by UV irradiation (254 nm).

Procedure for sulfonium salt synthesis by aryl-group transfer using mesityliodonium(III) salt 2. Diarylsulfide **1** (0.50 mmol), aryl(mesityl)iodonium(III) salt **2** (0.60 mmol, 1.2 equiv.) and $Cu(OAc)_2 \cdot H_2O$ (9.9 mg, 0.05 mmol, 10 mol % relative to diarylsulfide **1**) were dissolved in 1,2-dichloroethane (DCE, 5 mL) in a sealed tube. The reaction mixture was stirred at the indicated temperature and time (see Table 1). It was then cooled to room temperature, and the resulting solution was purified by column chromatography on silica gel (dichloromethane/acetone) to give triarylsulfonium triflate **3**. Sulfonium salts are generally light sensitive, and coloration of the compounds would occur during the column chromatography and evaporation.

(4-Methylphenyl)diphenylsulfonium triflate (3aa).[27] Gray solid; mp 97-98 °C. IR: 3064, 2928, 1591, 1476 cm^{-1}. ^1H NMR: δ 2.46 (s, 3H, CH_3), 7.49 (d, J 8.3 Hz, 2H, ArH), 7.61 (d, J 8.8 Hz, 2H, ArH), 7.68-7.76 (m, 10H, ArH) ppm. ^{13}C NMR: δ 21.0, 120.7 (q, J_{CF} 320.0 Hz, OTf), 121.4, 125.5, 131.1, 131.3, 131.4, 131.9, 134.2, 145.5 ppm.

Triphenylsulfonium triflate (3ab).[7] Orange solid; mp 130-133°C. IR: 3064, 1582, 1476 cm^{-1}. ^1H NMR: δ 7.68-7.79 (m, 15H, ArH) ppm. ^{13}C NMR: δ 120.7 (q, J_{CF} 320.0 Hz, OTf), 125.1, 131.2, 131.3, 134.3 ppm.

(4-Methoxyphenyl)diphenylsulfonium triflate (3ac).[7] White solid; mp 84-85 °C. IR: 3095, 2845, 1588, 1496 cm^{-1}. ^1H NMR: δ 3.90 (s, 3H, CH_3), 7.20 (d, J 9.3 Hz, 2H, ArH), 7.68-7.76 (m, 12H, ArH) ppm. ^{13}C NMR: δ 56.1, 114.0, 117.0, 120.7 (q, J_{CF} 321.0 Hz, OTf), 126.1, 130.7, 131.2, 133.9, 134.0, 163.9 ppm.

(4-Fluorophenyl)diphenylsulfonium triflate (3ad).[28] Gray solid; mp 111-115 °C. IR: 3062, 1588, 1493 cm^{-1}. ^1H NMR: δ 7.37-7.41 (m, 2H, ArH), 7.67-7.78 (m, 10H, ArH), 7.84-7.87 (m, 2H, ArH), ppm. ^{13}C NMR: δ 118.7 (d, J 23.1 Hz, Ar), 120.6 (d, J 3.3 Hz, Ar), 120.7 (q, J_{CF} 321.0 Hz, OTf), 125.3, 131.1, 131.3, 134.3, 134.6 (d, J 10.0 Hz, Ar), 165.3 (d, J 250.0 Hz, Ar) ppm. The same colored compound was obtained without the copper catalysis.

[4-(Methoxycarbonyl)phenyl]diphenylsulfonium triflate (3ae).[7] White solid; mp 78 °C. IR: 3064, 2955, 1730, 1595, 1447 cm^{-1}. ^1H NMR: δ 3.97 (s, 3H, CH_3), 7.70-7.82 (m, 12H, ArH), 8.30 (d, J 8.8 Hz, 2H, ArH) ppm. ^{13}C NMR: δ 52.9, 120.7 (q, J_{CF} 320.0 Hz, OTf), 124.8, 130.5, 131.4, 131.5, 131.7, 134.2, 134.6, 164.9 ppm.

(4-Cyanophenyl)diphenylsulfonium triflate (3af). Yellow viscous liquid. IR: 3092, 2235, 1595, 1476 cm^{-1}. ^1H NMR: δ 7.72-7.84 (m, 10H, ArH), 7.90 (d, J 9.3 Hz, 2H, ArH), 7.95 (d, J 8.8 Hz, 2H, ArH) ppm. ^{13}C NMR: δ 116.4, 117.3, 120.7 (q, J_{CF} 321.0 Hz, OTf), 124.6, 130.6, 131.2, 131.5, 131.8, 131.8, 134.7 ppm. HRMS (DART) calcd for $C_{19}H_{14}NS^+$ $[M\ -OTf]^+$ 288.0841, found 288.0842.

2-Naphthalenyldiphenylsulfonium triflate (3ag).[29] Brown viscous liquid. IR: 3061, 1581, 1502, 1476 cm^{-1}. ^1H NMR: δ 7.56 (dd, J 8.8 Hz, 2.0 Hz, 1H, ArH), 7.63-7.77 (m, 12H, ArH), 7.94 (d, J 8.3 Hz, 1H, ArH), 8.02 (d, J 8.8 Hz, 1H, ArH), 8.12 (d, J 9.3 Hz, 1H, ArH), 8.51 (d, J 2.0 Hz, 1H, ArH) ppm. ^{13}C NMR: δ 120.7 (q, J_{CF} 321.0 Hz, OTf), 121.9, 124.7, 125.4, 128.2, 128.5, 129.1, 130.3, 131.3, 131.4, 131.6, 132.5, 134.1, 134.3, 134.6 ppm.

(2-Furyl)diphenylsulfonium triflate (3ah). Gray solid; mp 68-70 °C. IR: 3093, 1589, 1497 cm^{-1}. ^1H NMR: δ 6.78-6.80 (m, 1H, ArH), 7.64-7.69 (m, 4H, ArH), 7.71-7.76 (m, 2H, ArH), 7.82-7.84 (m, 4H, ArH), 7.99-8.00 (m, 1H, ArH), 8.03-8.04 (m, 1H, ArH) ppm. ^{13}C NMR: δ 114.0, 120.7 (q, J_{CF} 320.0 Hz, OTf), 126.0, 128.1, 129.3, 130.6, 131.3, 134.2, 154.0 ppm. HRMS (DART) calcd for $C_{16}H_{13}OS^+$ $[M\ -\ OTf]^+$ 253.0682, found 253.0681.

Diphenyl(2-thienyl)sulfonium triflate (3ai).[7] Black solid; mp 94-96 °C. IR: 3090, 1580, 1476 cm^{-1}. ^1H NMR: δ 7.37-7.40 (m, 1H, ArH), 7.66-7.70 (m, 4H, ArH), 7.73-7.79 (m, 6H, ArH), 8.04 (dd, J 5.4, 1.5 Hz, 1H, ArH), 8.27 (dd, J 3.9, 1.5 Hz, 1H, ArH) ppm. ^{13}C NMR: δ 120.1, 120.7 (q, J_{CF} 321.0 Hz, OTf), 127.8, 129.9, 130.3, 131.3, 134.3, 140.0, 141.0 ppm.

Diphenyl(2,4,6-trimethoxyphenyl)sulfonium triflate (3aj).[30] Black viscous liquid. IR: 3094, 2951, 1596, 1475 cm^{-1}. ^1H NMR: δ 3.81 (s, 6H, CH_3), 3.98 (s, 3H, CH_3), 6.35 (s, 2H, ArH), 7.55 (d, J 7.8 Hz, 4H, ArH), 7.64 (t, J 7.6 Hz, 4H, ArH), 7.70 (t, J 7.1 Hz, 2H, ArH) ppm. ^{13}C NMR: δ 56.6, 57.1, 87.0, 93.4, 120.8 (q, J_{CF} 320.0 Hz, OTf), 125.0, 129.9, 130.9, 133.4, 162.3, 168.6 ppm. The same colored compound was obtained without the copper catalysis.

Bis(4-bromophenyl)phenylsulfonium triflate (3bb).[31] Orange solid; mp 108-110 °C. IR: 3087, 1566, 1473 cm^{-1}. ^1H NMR: δ 7.66 (d, J 8.8 Hz, 4H, ArH), 7.70-7.80 (m, 5H, ArH), 7.84 (d, J 8.8 Hz, 4H, ArH) ppm. ^{13}C NMR: δ 120.7 (q, J_{CF} 321.0 Hz, OTf), 124.5, 124.8, 128.8, 131.4, 131.4, 133.2, 134.3, 134.5 ppm.

Bis(4-methoxyphenyl)phenylsulfonium triflate (3cb).[7] Brown solid; mp 109-110 °C. IR: 3097, 2844, 1589, 1496 cm^{-1}. ^{1}H NMR: δ 3.90 (s, 6H, CH_3), 7.19 (d, J 9.3 Hz, 4H, ArH), 7.60-7.72 (m, 9H, ArH) ppm. ^{13}C NMR: δ 56.1, 115.1, 116.9, 120.7 (q, J_{CF} 321.0 Hz, OTf), 127.0, 130.2, 131.2, 133.4, 133.7, 163.8 ppm.

Bis(4-trifluoromethylphenyl)phenylsulfonium triflate (3db). Red solid; mp 150-153 °C. IR: 3096, 1605, 1448 cm^{-1}. ^{1}H NMR: δ 7.76 (t, J 7.8 Hz, 2H, ArH), 7.82-7.85 (m, 3H, ArH), 7.96 (d, J 8.8 Hz, 4H, ArH), 7.99 (d, J 9.3 Hz, 4H, ArH) ppm. ^{13}C NMR: δ 120.7 (q, J_{CF} 321.0 Hz, OTf), 123.2 (q, J 270.0Hz, CF_3), 124.2, 128.1 (q, J 4.0 Hz, Ar), 130.3, 131.6, 132.2, 132.6, 133.9 (q, J 30.0 Hz, Ar), 134.9 ppm. HRMS (DART) calcd for $C_{21}H_{14}F_9O_3S_2^+$ [M - OTf]$^+$ 399.0637, found 399.0635.

Bis(4-nitrophenyl)phenylsulfonium triflate (3eb). Yellow solid; mp 110-114 °C. IR: 3108, 1606, 1531, 1476 cm^{-1}. ^{1}H NMR: δ 7.75-7.82 (m, 4H, ArH), 7.87 (t, J 7.1 Hz, 1H, ArH), 7.99 (d, J 9.3 Hz, 4H, ArH), 8.50 (d, J 9.3 Hz, 4H, ArH) ppm. ^{13}C NMR: δ 120.7 (q, J_{CF} 321.0 Hz, OTf), 124.2, 125.9, 131.6, 132.1, 132.3, 133.2, 135.1, 150.6 ppm. HRMS (DART) calcd for $C_{19}H_{14}F_3N_2O_7S_2^+$ [M - OTf]$^+$ 353.0591, found 353.0589.

(4-Nitrophenyl)diphenylsulfonium triflate (3fb).[7] Yellow solid; mp 95-96 °C. IR: 3064, 1606, 1534, 1476 cm^{-1}. ^{1}H NMR: δ 7.72-7.76 (m, 4H, ArH), 7.80-7.84 (m, 6H, ArH), 7.98 (d, J 9.3 Hz, 2H, ArH), 8.46 (d, J 9.3 Hz, 2H, ArH) ppm. ^{13}C NMR: δ 120.6 (q, J_{CF} 321.0 Hz, OTf), 124.6,125.7, 131.4, 131.7, 132.4, 132.5, 134.7, 150.4 ppm.

Bis(2,4-dimethylphenyl)phenylsulfonium triflate (3hb).[28] Red solid; mp 121-126 °C. IR: 3061, 2921, 1602, 1447 cm^{-1}. ^{1}H NMR: δ 2.42 (s, 6H, CH_3), 2.50 (s, 6H, CH_3), 6.89 (d, J 8.3 Hz, 2H, ArH), 7.27 (d, J 8.8 Hz, 2H, ArH), 7.33 (s, 2H, ArH), 7.64 (d, J 8.3 Hz, 2H, ArH), 7.73 (t, J 7.6 Hz, 2H, ArH), 7.79 (t, J 7.3 Hz, 1H, ArH) ppm. ^{13}C NMR: δ 19.1, 21.0, 119.3, 120.8 (q, J_{CF} 320.0 Hz, OTf), 122.4, 130.1, 130.3, 131.5, 131.9, 133.7, 134.8, 140.4, 145.6 ppm.

Diphenyl(*o*-tolyl)sulfonium triflate (3ak).[28] ^{1}H NMR: δ 2.57 (s, 3H, CH_3), 7.07 (d, J 8.3, 1H, ArH), 7.46-7.52 (m, 2H, ArH), 7.63-7.81 (m, 11H, ArH) ppm. This compound was obtained as an inseparable mixture with mesityl(*o*-tolyl)iodonium(III) triflate **2k**.

Acknowledgements

N.T. and T.D. acknowledge support from JSPS KAKENHI Grant Number 20K06980 (N.T.) and 19K05466 (T.D.), and the Ritsumeikan Global Innovation Research Organization (R-GIRO) project. R.K. is thankful to the J C Bose University of Science and Technology, YMCA, Faridabad (Seed Grant R&D/SG/2020-21/166) and HSCSIT, Science and Technology Department, Haryana (HSCSIT/R&D/2021/2935).

Supplementary Material

Supplementary data associated with this article is available in the Supplementary Material.

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