Facile Method for the Preparation of Triarylsulfonium Bromides Using Grignard Reagents and Chlorotrimethylsilane as an Activator

Shigeaki Imazeki,*[a] Motoshige Sumino,[a] Kazuhito Fukasawa,[a] Masami Ishihara,[a] Takahiko Akiyama[b]

[a] Chemical Products Research Laboratories, Wako Pure Chemical Industries, Ltd., 1633 Matoba, Kawagoe, Saitama 350-1101, Japan
Fax +81(49)2337953; E-mail: imazeki.shigeaki@wako-chem.co.jp

[b] Department of Chemistry, Faculty of Science, Gakushuin University, 1-5-1 Mejiro, Toshima-ku, Tokyo 171-8588, Japan

Received 8 March 2004; revised 12 April 2004

Abstract: Triarylsulfonium bromides were synthesized by the reaction of diaryl sulfoxides with aryl Grignard reagents in the presence of TMSCl followed by treatment with HBr aqueous solution. Triarylsulfonium bromides bearing three identical substituents on sulfur atom were synthesized by the treatment of dimethyl sulfite or thionyl chloride with 5 equivalents of Grignard reagent in the presence of TMSCl.

Key words: silicon, Grignard reaction, sulfoxide, photo acid generator, coupling

Introduction

Triarylsulfonium salts have been extensively employed in industry as acid generators in photolithography and as photoinitiators in cationic polymerization because they produce protic acids upon irradiation.[1] Triarylsulfonium bromides are important precursors of triarylsulfonium salts because bromide anions could be readily transformed into various kinds of counter anions such as BF_4, SbF_6, PF_6. Development of the novel and efficient method for the preparation of triarylsulfonium bromides has been thus desired for the rapid progress of the information technology.

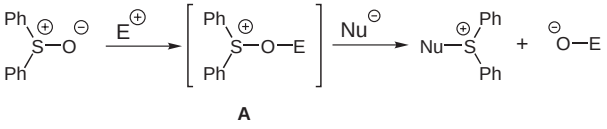
A number of synthetic methods for triarylsulfonium salts have been reported. For example, Okamoto and co-workers employed Pummerer type reaction, but mixtures of *o*- and *p*-isomers of triarylsulfonium salts were obtained.[2]

Although triarylsulfonium bromides have been synthesized by the reaction of diaryl sulfoxide with aryl lithium or aryl Grignard reagents, these procedures have drawbacks such as moderate chemical yields and the employment of harsh conditions.[3] In order to overcome these drawbacks, several activators have been investigated. For example, Andersen reported the reaction of diaryl sulfoxide with phenylmagnesium bromide under mild conditions in the presence of $Et_3O{\cdot}BF_4$.[4] Ito and co-workers reported the synthesis of triarylsulfonium bromides in the presence of trimethylsilyl bromide (TMSBr) as an activator at low temperature.[5] However $Et_3O{\cdot}BF_4$ is expensive, unstable, and harmful, and in Ito's method, the yields were moderate. The above-mentioned methods are not suitable for large-scale synthesis.

We wish to report herein a facile method for the preparation of triarylsulfonium bromides using readily available TMSCl as an activator in place of $Et_3O{\cdot}BF_4$.[6,7] Furthermore, a one-pot synthesis of triarylsulfonium bromides having the same substituents was achieved by the treatment of dimethyl sulfite or thionyl chloride with an excess of Grignard reagent and the addition of TMSCl to the resulting sulfoxide in situ.

Results and Discussion

Activation of sulfoxide moiety will generate active species **A**, which undergoes substitution reaction by nucleophile to give sulfonium salts (Scheme 1).



A

Scheme 1 Working hypothesis

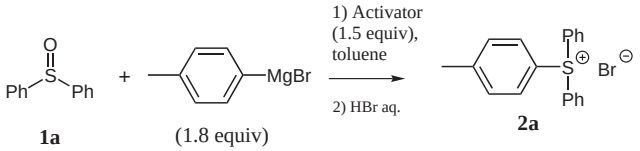
At the outset, we screened several electrophilic reagents, which possess affinity to oxygen atom in order to generate active species **A** in the reaction of diphenyl sulfoxide with *p*-tolymagnesium bromide (Table 1).

Among various activators tested, the highest yield (36%) was obtained when chlorotrimethylsilane was used (entry 5). A sulfonium salt **2a** was obtained in 10% yield by use of triphenylphosphine as an activator (entry 4), but was contaminated with triphenylphosphine oxide. Lewis acids and alkylating agents were not effective (entries 2 and 3). Especially for the kilogram scale synthesis, TMSCl is superior to $Et_3O{\cdot}BF_4$ or TMSOTf because TMSCl is easier to handle and is readily available. We then examined the optimal quantity of Grignard reagent and TMSCl in order to improve the yield of **2a** as shown in Table 2.

Increase of the amount of TMSCl improved the yield of **2a** while further increase of the amount of TMSCl decreased the yield. The amount of the Grignard reagent was then examined by use of 2.5 equivalents of TMSCl. The best result was obtained when 2.5 equivalents of TMSCl

SYNTHESIS 2004, No. 10, pp 1648–1654
Advanced online publication: 23.06.2004
DOI: 10.1055/s-2004-829113; Art ID: F03504SS

Table 1 Examination of the Activator



1a (1.8 equiv) **2a**

Entry	Activator	Yield of **2a** (%)
1	None	trace
2	$Sc(OTf)_3$	0
3	$(MeO)_2SO_2$	0
4	Ph_3P	10[a]
5	TMSCl	36[a]
6	HMDS[b]	trace

[a] Isolated yield.
[b] HMDS = hexamethyldisilazane.

Table 2 Influence of the Amount of the Grignard Reagent and TMSCl

Entry	TMSCl (equiv)	Grignard (equiv)	Yield of **2a** (%)
1	1.5	1.8	36
2	2.0	1.8	50
3	2.5	1.8	53
4	3.0	1.8	46
5	2.5	1.5	40
6	2.5	2.5	73
7	2.5	3.0	74
8	2.5	4.0	74

and 2.5 equivalents of the Grignard reagent were used (entry 6).

Among the solvents tested, THF (the yield of **2a** was 71%) and toluene (73%) exhibited comparative results while Et_2O (65%), diisopropyl ether (10%), and dimethoxyethane (48%) were not effective.

Thus the facile method for the preparation of **2a** was accomplished by addition of TMSCl to the mixture of the Grignard reagent and **1a** at 25 ± 5 °C in THF, and the effect of the silyl substituent was examined under the optimized reaction conditions (Table 3). TMSBr also afforded **2a** in a good yield (entry 2) while TMSI gave triphenylsulfonium iodide (60%) in addition to **2a** (24%) (entry 3). Chlorosilanes bearing sterically hindered silyl group gave **2a** in poor yields (entries 6 and 7). These results indicate that TMSCl is the best activator since TMSCl can be handled easily and is economically viable.

Table 3 Effect of Silyl Substituents

Entry	Si	Yield of **2a** (%)
1	TMSCl	85
2	TMSBr	76
3	TMSI	24[a]
4	$Me_2PhSiCl$	88
5	Ph_3SiCl	20
6	*i*-Pr_3SiCl	1
7	*t*-$BuPh_2SiCl$	2[b]

[a] The iodide was obtained 60% yield.
[b] **1a** was recovered in 87% yield

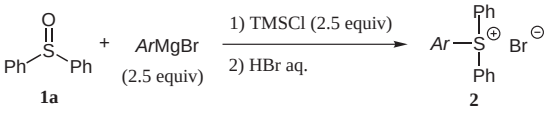
Finally, we examined the scope and limitations of the present reaction using TMSCl (Tables 4 and 5). When various Grignard reagents were used, the corresponding sulfonium bromides were obtained in good to excellent yields though sterically hindered Grignard reagents reduced the yield of **2** (entries 1–3). The yields of sulfonium bromides also decreased when Grignard reagents bearing an electron-withdrawing group on aromatic ring were used (Table 4, entries 12–14). This reduction of the yield was brought about by the poor nucleophilicity of electron-withdrawing group on Grignard reagents.

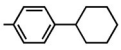
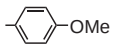
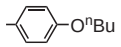
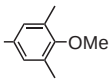
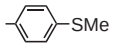
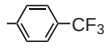
The reaction of phenylmagnesium bromide with various sulfoxides was studied (Table 5). Sulfoxides bearing electron-donating group afforded the corresponding sulfonium bromide in excellent yields (entries 2–4). On the other hand, a sulfoxide with electron-withdrawing group, which destabilized the positive charge on sulfur atom, slightly decreased the yield. A sulfonium bromide bearing hydroxy moiety was obtained in 69% yield when 4.7 equivalents of Grignard reagent was employed (entry 7).

Triarylsulfonium bromide was not obtained in the absence of TMSCl. On treatment of dimethyl sulfite (**4a**) or thionyl chloride (**4b**) with excess Grignard reagent followed by addition of TMSCl to the resulting sulfoxide in situ, the one-pot synthesis of triarylsulfonium bromides bearing the three identical substituents were accomplished (Table 6).

Both **4a** and **4b** gave comparative results. Grignard reagents bearing electron-donating group afforded the corresponding sulfonium bromides in good yields (entries 2–4) while use of the Grignard reagent bearing electronegative halogen atom slightly decreased the yields (entry 5). On the other hand, when dimethyl sulfite was used, the reaction took place smoothly under mild conditions while thionyl chloride reacted vigorously with Grignard reagent and the control of the reaction was somewhat difficult. Thus, dimethyl sulfite is considered to be superior to thionyl chloride due to the stability and the easiness of the handling.

Table 4 Synthesis of Sulfonium Bromide (I)



Entry	Ar	Product	Yield (%)
1		**2a**	85
2		**2b**	77
3		**2c**	64
4		**2d**	87
5		**2e**	79
6		**2f**	93
7		**2g**	91
8		**2h**	77
9		**2i**	78
10		**2j**	84
11		**2k**	83
12		**2l**	66
13		**2m**	66
14[a]		**2n**	72

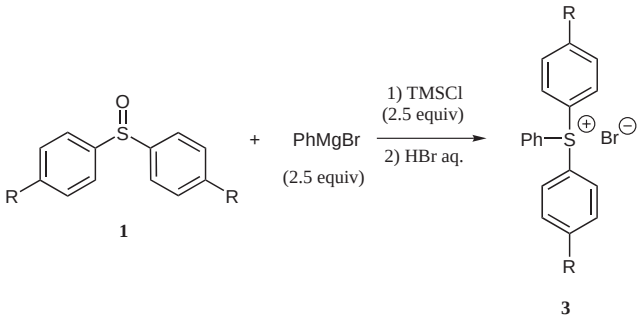
[a] Et_2O as a solvent was employed in this reaction.

Conclusion

We have found a facile method for the preparation of triarylsulfonium bromide from readily available diaryl sulfoxides by use of Grignard reagents in the presence of TMSCl as an activator. Furthermore, the one-pot synthesis of triarylsulfonium bromides having the same substituents was accomplished by treating dimethyl sulfite or thionyl chloride with 5 equivalents of Grignard reagent in the coexistence of TMSCl. It is noted that our protocol could be applied to large-scale synthesis of the sulfonium salts such as on the kilogram-scale.

NMR spectra were measured in $CDCl_3$ on 400 MHz spectrometers with TMS as the internal standard. $CDCl_3$ was used as an internal standard for ^{13}C NMR and chemical shift values of ^{19}F NMR are given in ppm relative to internal CF_3COOH. All reagents are commercially available from Wako Pure Chemical Industries Ltd., Japan.

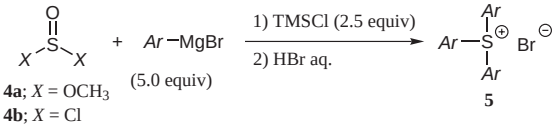
Table 5 Synthesis of Sulfonium Bromide (II)

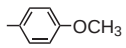


Entry	Sulfoxide	R	Product	Yield (%)
1	**1a**	H	**2d**	87
2	**1b**	CH_3	**3b**	90
3	**1c**	OCH_3	**3c**	94
4	**1d**	*t*-Bu	**3d**	91
5	**1e**	F	**3e**	72
6	**1f**	Cl	**3f**	66
7[a]	**1g**	OH	**3g**	69

[a] 4.7 equivalents of Grignard reagent was employed.

Table 6 Synthesis of Sulfonium Bromide (III)



Entry	Ar	Product	Yield /%
1		**2d**	50 (from **4a**) 42 (from **4b**)
2		**5b**	73 (from **4a**) 77 (from **4b**)
3		**5c**	68 (from **4a**) 68 (from **4b**)
4		**5d**	76 (from **4a**) 66 (from **4b**)
5		**5e**	46 (from **4a**) 51 (from **4b**)

Preparation of 4-Methylphenyldiphenylsulfonium Bromide (2a); Typical Procedure

Grignard reagent was prepared from 4-bromotoluene and magnesium in THF according to the standard procedure. Sulfoxide **1a** (3.38 g, 16.7 mmol) was added to the Grignard reagent (29 mL, 41.8 mmol, 1.45 mol/L) at r.t. and then TMSCl (4.54 g, 41.8 mmol) added to the mixture keeping the temperature at 25 ± 5 °C. After being

stirred for 30 min, the reaction was quenched by addition of aq HBr solution. The organic layer was extracted with HBr solution. The combined water layers were extracted with CH_2Cl_2 and the combined CH_2Cl_2 layer was washed with brine, dried over anhyd Na_2SO_4, and concentrated to dryness. Purification of the crude mixture by recrystallization (*i*-PrOH–hexanes) gave **2a** as white crystals (5.09g, 14.2 mmol, 85%); mp 243.1–243.6 ºC; R_f = 0.3 (CH_2Cl_2–MeOH, 9:1).

IR (KBr): 3069, 3045, 2984, 2359, 1591, 1475, 1446, 1309, 1188, 1155, 1066, 995, 808, 763, 686 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.84–7.71(m, 12 H, Ph), 6.73(d, *J* = 8.5 Hz, 2 H, Ph), 2.48 (s, 3 H, CH_3).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 145.67, 133.91, 131.79, 131.03, 130.87, 130.58, 124.11, 119.88, 21.39.

LC–MS (ESI): *m*/*z* (%) = 277 (80), 199 (100), 90 (15), 78 (10).

UV (MeOH): λ_{max} = 204 (51290), 238 nm (19884).

Anal. Calcd for $C_{19}H_{17}BrS$: C, 63.87; H, 4.80. Found: C, 63.97; H, 4.67.

3-Methylphenyldiphenylsulfonium Bromide (2b)
White crystals; mp 126.7–128.0 ºC (*i*-PrOH–hexanes); R_f = 0.3 (CH_2Cl_2–MeOH, 9:1).

IR (KBr): 3440, 3079, 3030, 1622, 1599, 1476, 1445, 1317, 1068, 995, 789, 767, 750, 684 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.87–7.84 (m, 4 H, Ph), 7.82–7.72 (m, 6 H, Ph), 7.64–7.57 (m, 4 H, Ph), 2.46 (s, 3 H, CH_3).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 141.80, 135.02, 134.08, 131.12, 130.92, 130.82, 130.79, 127.78, 124.11, 123.73, 21.32.

LC–MS (ESI): *m*/*z* (%) = 277 (100), 200 (20), 186 (20).

UV (MeOH): λ_{max} = 204 (50875), 235 nm (17174).

Anal. Calcd for $C_{19}H_{17}BrS$: C, 63.87; H, 4.80. Found: C, 63.58; H, 5.05.

2-Methylphenyldiphenylsulfonium Bromide (2c)
White crystals; mp 228.6–228.9 ºC (*i*-PrOH–hexanes); R_f = 0.3 (CH_2Cl_2–MeOH, 9:1).

IR (KBr): 3476, 3404, 3077, 2993, 2338, 1591, 1473, 1446, 1278, 1178, 1159, 1072, 995, 765, 688 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.86–7.73 (m, 10 H, Ph), 7.68–7.65 (m, 1 H, Ph), 7.55–7.32 (m, 2 H, m, Ph), 7.09 (d, *J* = 8.3 Hz, 1 H, Ph), 2.66 (s, 3 H, CH_3).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 140.69, 134.40, 134.20, 133.03, 131.49, 131.35, 129.56, 128.78, 123.53, 122.93, 20.43.

LC–MS (ESI): *m*/*z* (%) = 277 (90), 199 (30), 186 (100), 93 (90), 76 (30).

UV (MeOH): λ_{max} = 204 (45637), 235 nm (18031).

Anal. Calcd for $C_{19}H_{17}BrS$: C, 63.87; H, 4.80. Found: C, 64.01; H, 4.85.

Triphenylsulfonium Bromide (2d)
White crystals; mp 290.5–290.9 ºC (*i*-PrOH–hexanes); R_f = 0.3 (CH_2Cl_2–MeOH, 9:1).

IR (KBr): 3072, 3045, 2984, 1577, 1477, 1446, 1309, 1155, 1064, 995, 769, 752, 686 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.88–7.73 (m, 15 H, Ph).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 133.88, 130.89, 130.52, 123.78.

LC–MS (ESI): *m*/*z* (%) = 263 (100), 186 (20), 77 (15).

UV (MeOH): λ_{max} = 205 (41253), 233 nm (17498).

Anal. Calcd for $C_{18}H_{15}BrS$: C, 62.98; H, 4.40. Found: C, 62.96; H, 4.56.

4-*t*-Butylphenyldiphenylsulfonium Bromide (2e)
White crystals; mp 232.0–233.2 ºC (EtOAc); R_f = 0.4 (CH_2Cl_2–MeOH, 9:1).

IR (KBr): 3045, 2966, 1587, 1473, 1444, 1396, 1363, 1309, 1267, 1194, 1178, 1113, 1072, 995, 852, 823, 763, 688 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.87–7.70 (m, 14 H, Ph), 1.35 [s, 9 H, $(CH_3)_3$].

^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.45, 134.02, 131.116, 131.01, 130.82, 128.37, 124.73, 120.51, 35.35, 30.78.

LC–MS (ESI): *m*/*z* (%) = 319 (100), 241 (100), 186 (40), 166 (60).

UV (MeOH): λ_{max} = 204 (49326), 238 nm (19198).

Anal. Calcd for $C_{22}H_{23}BrS$: C, 66.16; H, 5.80. Found: C, 66.19; H, 5.79.

4-Cyclohexylphenyldiphenylsulfonium Bromide (2f)
White crystals; mp 147.2–148.8 ºC (hexanes); R_f = 0.3 (CH_2Cl_2–MeOH, 10:1).

IR (KBr): 3412, 3344, 3053, 2924, 2851, 2091, 1585, 1475, 1444, 1410, 1327, 1186, 1111, 1068, 1022, 997, 835, 754, 684 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.85–7.54 (m, 12 H, Ph), 7.54–7.51 (m, 2 H, Ph), 2.61 (dt, *J* = 6.4, 2.4 Hz, 1 H, CH), 1.95–1.81 (m, 4 H, CH_2), 1.76 (dddd, *J* = 1.5, 2.7, 8.0, 13.0 Hz, 1 H, CH_2), 1.30–1.19 (m, 4 H, CH_2), 1.25 (dddd, *J* = 3.1, 7.2, 8.7, 25.6 Hz, 1 H, CH_2).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 155.74, 134.43, 131.74, 131.58, 131.31, 130.24, 125.32, 121.08, 44.83, 34.23, 26.84, 26.15.

LC–MS (ESI): *m*/*z* (%) = 345 (100), 267 (90), 191 (40).

UV (MeOH): λ_{max} = 204 (52786), 240 nm (20250).

Anal. Calcd for $C_{24}H_{25}BrS$: C, 67.76; H, 5.92. Found: C, 67.62; H, 5.93.

4-Methoxyphenyldiphenylsulfonium Bromide (2g)
White crystals; mp 155.0–156.3 ºC (*i*-PrOH–hexanes); R_f = 0.4 (CH_2Cl_2–MeOH, 12:1).

IR (KBr): 3481, 3393, 3080, 2841, 2575, 2019, 1587, 1495, 1475, 1444, 1415, 1311, 1269, 1178, 1116, 1070, 1016, 939, 856, 837, 798, 756, 686 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.89 (dd, *J* = 2.0, 7.1 Hz, 2 H, Ph), 7.80–7.68 (m, 10 H, Ph) 7.23 (dd, *J* = 2.0, 7.1 Hz, 2 H, Ph), 3.92 (s, 3 H, CH_3O).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 164.24, 133.91, 133.65, 131.15, 130.48, 125.37, 117.08, 112.92, 56.18.

LC–MS (ESI): *m*/*z* (%) = 292 (20), 279 (100), 217 (30), 139 (15).

UV (MeOH): λ_{max} = 204 (49550), 261 nm (18006).

Anal. Calcd for $C_{19}H_{17}BrOS$: C, 61.13; H, 4.59. Found: C, 61.50; H, 4.59.

3-Methoxyphenyldiphenylsulfonium Bromide (2h)
White crystals.; mp 88.4–89.8 ºC (*i*-PrOH–hexanes); R_f = 0.3 (CH_2Cl_2–MeOH, 9:1).

IR (KBr): 3466, 3387, 3084, 3032, 3015, 2976, 2839, 1591, 1483, 1444, 1427, 1286, 1250, 1188, 1072, 1032, 997, 875, 785, 761, 684 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.89–7.83 (m, 4 H, Ph), 7.80–7.67 (m, 6 H, Ph), 7.63 (s, 1 H, Ph), 7.59 (t, *J* = 8.2 Hz, 1 H, Ph), 7.25 (d, *J* = 8.2 Hz, 1 H, Ph), 7.21 (d, *J* = 8.2 Hz, 1 H, Ph), 3.89 (s, 3 H, OCH_3).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.06, 134.22, 132.00, 131.23, 131.14, 125.46, 124.54, 122.38, 120.56, 116.65, 56.49.

LC–MS (ESI): *m*/*z* (%) = 279 (80), 264 (100), 216 (15).

UV (MeOH): λ_{max} = 203 (48774), 292 nm (4055).

Anal. Calcd for $C_{19}H_{17}BrOS$: C, 61.13; H, 4.59. Found: C, 61.01; H, 4.90.

4-*n*-Butoxyphenyldiphenylsulfonium Bromide (2i)
White crystals; mp 130.4–132.5 ºC (*i*-PrOH–hexanes); R_f = 0.3 (CH_2Cl_2–MeOH, 12:1).

IR (KBr): 3483, 3406, 3192, 3080, 3022, 2957, 2874, 2575, 1900, 1767, 1682, 1587, 1475, 1444, 1415, 1309, 1261, 1178, 1120, 1068, 1022, 999, 964, 856, 763, 688 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.87 (d, *J* = 8.8 Hz, 2 H, Ph), 7.80–7.68 (m, 10 H, Ph), 7.19 (d, *J* = 9.0 Hz, 2 H, Ph), 4.06 (t, *J* = 6.3 Hz, 2 H, OCH_2), 1.79 (dt, *J* = 6.3, 21.5 Hz, 2 H, CH_2), 1.49 (dq, *J* = 7.5, 21.5 Hz, 2 H, CH_2), 0.97 (t, *J* = 7.5 Hz, 3 H, CH_3).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 163.59, 1333.92, 133.77, 131.19, 130.59, 125.61, 117.46, 112.64, 68.76, 30.87, 19.12, 13.76.

LC–MS (ESI): *m*/*z* (%) = 335 (20), 279 (100), 258 (50), 217 (30), 202 (50).

UV (MeOH): λ_{max} = 204 (40780), 263 nm (12945).

Anal. Calcd for $C_{22}H_{23}BrOS$: C, 63.61; H, 5.58%. Found: C, 63.51; H, 5.60.

4-Methoxy-3,5-dimethylphenyldiphenylsulfonium Bromide (2j)
White crystals; mp 174.2–175.2 ºC (*i*-PrOH–hexanes); R_f = 0.3 (CH_2Cl_2–MeOH, 9:1).

IR (KBr): 3474, 3406, 3047, 3005, 2982, 2918, 1574, 1475, 1446, 1402, 1313, 1275, 1230, 1169, 1111, 1072, 999, 893, 767, 752, 684 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.86–7.41 (m, 4 H, Ph), 7.75–7.69 (m, 6 H, Ph), 7.50 (s, 2 H, Ph), 3.81 (s, 3 H, OCH_3), 2.35 (s, 6 H, CH_3).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.17, 135.30, 134.09, 131.69, 131.28, 131.01, 125.17, 117.47, 60.05, 16.72.

LC–MS (ESI): *m*/*z* (%) = 321 (30), 307 (60), 245 (20), 230 (100).

UV (MeOH): λ_{max} = 204 (57704), 255 nm (15151).

Anal. Calcd for $C_{21}H_{21}BrOS$: C, 62.84; H, 5.27. Found: C, 62.85; H, 5.33.

Diphenyl-4-methylthiophenylsulfonium Bromide (2k)
White crystals; mp 160.8–161.8 ºC (*i*-PrOH–hexanes); R_f = 0.3 (CH_2Cl_2–MeOH, 12:1).

IR (KBr): 3447, 3045, 2990, 2943, 1566, 1547, 1475, 1441, 1402, 1313, 1201, 1178, 1099, 1062, 997, 825, 804, 761, 748, 682 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.86–7.78 (m, 6 H, Ph), 7.76–7.69 (m, 6 H, Ph), 7.48 (d, *J* = 8.5 Hz, 2 H, Ph), 2.53 (s, 3 H, CH_3S).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 149.17, 134.02, 131.44, 131.18, 130.67, 127.17, 124.85, 117.94, 14.75.

LC–MS (ESI): *m*/*z* (%) = 309 (90), 233 (100), 218 (80), 156 (40).

UV (MeOH): λ_{max} = 204 (47465), 302 nm (22930).

Anal. Calcd for $C_{19}H_{17}BrS_2$: C, 58.61; H, 4.40. Found: C, 56.82; H, 4.54.

4-Fluorophenyldiphenylsulfonium Bromide (2l)
White crystals; mp 222.0–223.2 ºC (*i*-PrOH–hexanes); R_f = 0.3 (CH_2Cl_2–MeOH, 12:1).

IR (KBr): 3466, 3071, 3015, 2986, 1587, 1491, 1446, 1404, 1309, 1240, 1165, 1103, 1066, 995, 844, 815, 756, 686 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.11–8.07 (m, 2 H, Ph), 7.88–7.86 (m, 4 H, Ph), 7.79–7.69 (m, 6 H, Ph), 7.44–7.39 (m, 2 H, Ph).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.37, 164.79, 134.89, 134.79, 134.61, 131.68, 131.36, 125.14, 120.23, 119.39, 119.15.

^{19}F NMR (376 MHz, $CDCl_3$): δ = –99.89.

LC–MS (ESI): *m*/*z* (%) = 281 (100), 203 (60), 185 (40), 77 (15).

UV (MeOH): λ_{max} = 204 (47073), 234 nm (17709).

Anal. Calcd for $C_{18}H_{14}BrFS$: C, 59.84; H, 3.91. Found: C, 59.86; H, 4.08.

4-Chlorophenyldiphenylsulfonium Bromide (2m)
White crystals; mp 221.6–222.6 ºC (*i*-PrOH–hexanes); R_f = 0.3 (CH_2Cl_2–CH_3OH, 9:1).

IR (KBr): 3478, 3069, 3003, 2953, 1570, 1475, 1446, 1400, 1313, 1282, 1184, 1091, 1068, 1008, 997, 933, 841, 815, 754, 684 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.05–7.73 (m, 6 H, Ph), 7.72–7.61 (m, 8 H, Ph).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 141.13, 134.30, 132.71, 131.41, 131.30, 130.98, 124.14, 122.74.

LC–MS (ESI): *m*/*z* (%) = 297 (100), 263 (70), 219 (80).

UV (MeOH): λ_{max} = 204 (47858), 239 nm (21492).

Anal. Calcd for $C_{18}H_{14}BrClS$: C, 57.24; H, 3.74. Found: C, 57.28; H, 3.78.

Diphenyl-4-trifluoromethylphenylsulfonium Bromide (2n)
Pale yellow crystals; mp 108.1–110.7 ºC (*i*-PrOH–hexanes); R_f = 0.3 (CH_2Cl_2–MeOH, 4:1).

IR (KBr): 3439, 3026, 1604, 1477, 1446, 1402, 1325, 1176, 1134, 1060, 1010, 844, 752, 702, 684 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.18 (d, *J* = 8.3 Hz, 2 H, Ph), 7.96–7.94 (m, 6 H, Ph), 7.82–7.72 (m, 6 H, Ph).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 135.68, 135.35, 134.65, 132.06, 131.51, 131.47, 129.55, 127.97, 127.94, 123.85, 121.11.

^{19}F NMR (376 MHz, $CDCl_3$): δ = –64.48.

LC–MS (ESI): *m*/*z* (%) = 331 (100), 263 (30), 178 (15).

UV (MeOH): λ_{max} = 204 (45223), 233 nm (18415).

Anal. Calcd for $C_{19}H_{14}BrF_3S$: C, 55.49; H, 3.43. Found: C, 55.32; H, 3.39.

Bis(4-methylphenyl)phenylsulfonium Bromide (3b)
White crystals; mp 207.8–208.9 ºC (*i*-PrOH–hexanes); R_f = 0.3 (CH_2Cl_2–MeOH, 15:1).

IR (KBr): 3617, 3065, 3003, 2955, 1589, 1491, 1443, 1402, 1315, 1290, 1213, 1186, 1124, 1068, 1014, 825, 806, 760, 688 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.78 (d, *J* = 7.8 Hz, 2 H, Ph), 7.73–7.68 (m, 7 H, Ph), 7.48 (d, *J* = 8.6 Hz, 4 H, Ph), 2.45 (s, 6 H, CH_3).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 145.64, 133.94, 131.93, 131.15, 130.94, 130.66, 125.17, 120.97, 21.63.

LC–MS (ESI) *m*/*z* (%) = 219 (100), 213 (100), 199 (45), 123 (30).

UV (MeOH): λ_{max} = 204 (54869), 241 nm (22077).

Anal. Calcd for $C_{20}H_{19}BrS$: C, 64.69; H, 5.16. Found: C, 64.52; H, 5.00.

Bis(4-methoxyphenyl)phenylsulfonium Bromide (3c)
Colorless oil; R_f = 0.3 (CH_2Cl_2–MeOH, 12:1).

IR (neat): 3400, 3086, 2976, 2841, 2575, 1589, 1495, 1445, 1416, 1311, 1271, 1180, 1126, 1076, 1018, 837, 798, 752, 686 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.81 (d, *J* = 8.8 Hz, 4 H, Ph), 7.72–7.69 (m, 5 H, Ph), 7.20 (d, *J* = 8.8 Hz, 4 H, Ph), 3.90 (s, 6 H, OCH_3).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 164.08, 133.60, 133.17, 131.07, 129.98, 126.38, 117.03, 114.17, 56.21.

LC–MS (ESI): *m*/*z* (%) = 323 (100), 246 (10), 201 (80).

UV (MeOH): λ_{max} = 206 (41862), 259 nm (23105).

Anal. Calcd for $C_{20}H_{19}BrO_2S$: C, 59.56; H, 4.75. Found: C, 59.52; H, 4.69.

Bis(4-t-butylphenyl)phenylsulfonium Bromide (3d)
White crystals; mp 245.6–245.9 ºC (EtOAc–hexanes); R_f = 0.3 (CH_2Cl_2–MeOH, 15:1).

IR (KBr): 3067, 2964, 2872, 1587, 1493, 1471, 1446, 1400, 1363, 1269, 1203, 1117, 1072, 1009, 997, 850, 837, 767, 690 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.86–7.82 (m, 6 H, Ph), 7.76–7.71 (m, 7 H, Ph), 1.35 (s, 18 H, CH_3).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.97, 133.66, 130.88, 130.59, 130.35, 128.05, 124.74, 120.63, 35.05, 30.54.

LC–MS (ESI): *m*/*z* (%) = 375 (100), 185 (50).

UV (MeOH): λ_{max} = 202 (61996), 242 nm (24722).

Anal. Calcd for $C_{26}H_{31}BrS$: C, 68.56; H, 6.86. Found: C, 68.61; H, 6.89.

Bis(4-fluorophenyl)phenylsulfonium Bromide (3e)
White crystals; mp 241.6–242.1 ºC (*i*-PrOH–hexanes); R_f = 0.3 (CH_2Cl_2–MeOH, 9:1).

IR (KBr): 3574, 3480, 3090, 3047, 3018, 2976, 1585, 1491, 1448, 1408, 1300, 1240, 1163, 1105, 1070, 1008, 848, 814, 756, 686 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 8.13–8.09 (m, 4 H, Ph), 7.89–7.86 (m, 2 H, Ph), 7.79–7.70 (m, 3 H, Ph), 7.46–7.41(m, 4 H, Ph).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.02, 164.44, 134.41, 134.31, 131.41, 130.92, 130.80, 124.75, 119.84, 119.82, 119.14, 118.90.

^{19}F NMR (376 MHz, $CDCl_3$): δ = –100.22.

LC–MS (ESI): *m*/*z* (%) = 299 (70), 262 (75), 222 (30), 203 (50).

UV (MeOH): λ_{max} = 204 (48728), 234 nm (19024).

Anal. Calcd for $C_{18}H_{13}BrF_2S$: C, 57.00; H, 3.45. Found: C, 57.20; H, 3.45.

Bis(4-chlorophenyl)phenylsulfonium Bromide (3f)
White crystals; mp 179.3–180.4 ºC (EtOAc); R_f = 0.3 (CH_2Cl_2–MeOH, 9:1).

IR (KBr): 3069, 2984, 1570, 1475, 1446, 1394, 1309, 1157, 1039, 1064, 997, 829, 769, 746, 686 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 8.02–7.98 (m, 3 H, Ph), 7.92–7.76 (m, 2 H, Ph), 7.75–7.65 (m, 8 H, Ph).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 141.52, 134.53, 132.88, 131.64, 131.51, 131.14, 124.32, 122.84.

LC–MS (ESI): *m*/*z* (%) = 333 (80), 297 (100), 255 (40), 144 (10).

UV (MeOH): λ_{max} = 204 (55151), 243 nm (26465).

Anal. Calcd for $C_{18}H_{13}BrCl_2S$: C, 52.45; H, 3.18. Found: C, 52.42; H, 3.20.

Bis(4-hydroxyphenyl)phenylsulfonium Bromide (3g)
White powder; mp 252.6–253.0 ºC (*i*-PrOH–hexanes); R_f = 0.4 (CH_2Cl_2–MeOH, 4:1).

IR (KBr): 3061, 1595, 1579, 1496, 1441, 1342, 1288, 1224, 1174, 1109, 1072, 846, 744, 719, 679 cm^{-1}.

^1H NMR (400 MHz, CD_3OD): δ = 7.80–7.70 (m, 3 H, Ph), 7.64–7.62 (m, 6 H, Ph), 7.13–7.10 (m, 4 H, Ph), 3.30–3.29 (br d, 2 H, OH).

^{13}C NMR (100 MHz, CD_3OD): δ = 164.47, 134.64, 134.23, 132.11, 130.78, 128.52, 119.28, 114.05.

LC–MS (ESI): *m*/*z* (%) = 295 (80), 277 (100), 217 (80), 202 (70), 124 (20).

UV (MeOH): λ_{max} = 204 (54444), 260 nm (23336).

Anal. Calcd for $C_{18}H_{15}BrO_2S$: C, 57.61; H, 4.03. Found: C, 57.71; H, 4.01.

Tris(4-methylphenyl)sulfonium bromide (5b)
White crystals; mp 247.5–248.0 ºC (*i*-PrOH–hexanes); R_f = 0.3 (CH_2Cl_2–MeOH, 10:1).

IR (KBr): 3001, 2953, 1952, 1589, 1491, 1448, 1402, 1383, 1315, 1292, 1213, 1186, 1124, 1070, 1045, 1016, 825, 808, 704 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.69 (d, *J* = 8.3 Hz, 6 H, Ph), 7.49 (d, *J* = 8.3 Hz, 6 H, Ph), 2.46 (s, 9 H, CH_3).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 145.36, 131.77, 130.58, 121.16, 21.50.

LC–MS (ESI): *m*/*z* (%) = 305 (80), 213 (100).

UV (MeOH): λ_{max} = 204 (58696), 242 nm (25157).

Anal. Calcd for $C_{21}H_{21}BrS$: C, 65.45; H, 5.49. Found: C, 65.52; H, 5.48.

Tris(4-*tert*-butylphenyl)sulfonium Bromide (5c)
White powder; mp 276.0–276.5 ºC (EtOAc–hexanes); R_f = 0.4 (CH_2Cl_2–CH_3OH, 12:1).

IR (KBr): 3418, 3028, 2963, 2907, 2870, 2079, 1587, 1489, 1400, 1365, 1269, 1201, 1113, 1072, 1006, 839, 727 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.76 (d, *J* = 8.7 Hz, 6 H, Ph), 7.67 (d, *J* = 8.7 Hz, 6 H, Ph), 1.32 (s, 27 H, CH_3).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.15, 132.11, 130.86, 128.32, 121.53, 35.48, 30.99.

LC–MS (ESI): *m*/*z* (%) = 431 (100), 297 (30).

UV (MeOH): λ_{max} = 204 (56360), 243 nm (26823).

Anal. Calcd for $C_{30}H_{39}BrS$: C, 70.43; H, 7.68. Found: C, 70.18; H, 7.66.

Tris(4-methoxyphenyl)sulfonium Bromide (5d)
Colorless oil; R_f = 0.3 (CH_2Cl_2–MeOH, 9:1).

IR (neat): 3445, 3088, 3015, 2974, 2943, 2841, 1587, 1495, 1460, 1442, 1415, 1309, 1267, 1178, 1118, 1076, 1020, 835, 798, 729 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.70 (d, *J* = 8.8 Hz, 6 H, Ph), 7.18 (d, *J* = 8.8 Hz, 6 H, Ph), 3.91 (s, 9 H, CH_3O).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 163.91, 132.53, 116.90, 115.21, 56.12.

LC–MS (ESI): *m*/*z* (%) = 353 (20), 339 (100), 232 (25), 139 (10).

UV (MeOH): λ_{max} = 205 (51341), 259 nm (31013).

Anal. Calcd for $C_{21}H_{21}BrO_3S$: C, 58.20; H, 4.88. Found: C, 57.95; H, 4.84.

Tris(4-fluorophenyl)sulfonium Bromide (5e)
White crystals; mp 145.4–147.9 ºC (*i*-PrOH–hexanes); R_f = 0.3 (CH_2Cl_2–MeOH, 12:1).

IR (KBr): 3356, 3090, 3013, 2970, 1581, 1491, 1406, 1300, 1238, 1159, 1101, 1068, 1006, 841, 814 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 8.13–8.09 (m, 6 H, Ph), 7.46–7.41 (m, 6 H, Ph).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.04, 164.45, 134.25, 134.15, 119.89, 119.86, 119.20, 118.97.

^{19}F NMR (376 MHz, $CDCl_3$): δ = –99.75.

LC–MS (ESI): *m*/*z* (%) = 317 (100), 263 (20).

UV (MeOH): λ_{max} = 204 (40078), 235 nm (15298).

Anal. Calcd for $C_{18}H_{12}BrF_3S$: C, 54.42; H, 3.04. Found: C, 54.57; H, 3.04.

Acknowledgment

The authors are grateful to Drs. Shigeru Kobayashi and Toshio Watanabe for their helpful discussion.

References

(1) (a) DeVoe, R. J.; Olofson, P. M.; Sahyun, M. R. V. In *Advances in Photochemistry*, Vol. 17; Volman, D. H.; Hammond, G. S.; Neckers, D. C., Eds.; John Wiley and Sons: New York, **1992**, 313. (b) Ito, H.; Willson, C. G.; Frechet, J. M. *Angew. Digest Tech. Papers Symp. On VLSI Tech.* **1982**, 82. (c) Ito, H.; Willson, C. G. *Polym. Eng. Sci.* **1983**, *23*, 1012. (d) Ito, H.; Willson, C. G. *ACS Symp. Ser.* **1984**, *242*, 11.

(2) Endo, Y.; Shudo, K.; Okamoto, T. *Chem. Pharm. Bull.* **1981**, *29*, 3753.

(3) (a) Wildi, B. S.; Taylor, S. W.; Potratz, H. A. *J. Am. Chem. Soc.* **1951**, *73*, 1965. (b) Wiegand, G. H.; McEwern, W. E. *J. Org. Chem.* **1968**, *33*, 2671. (c) Nesmejanov, A. N.; Makarova, L. G.; Tolstaya, T. P. *Tetrahedron* **1957**, *1*, 145. (d) Crivello, J. V.; Lam, J. H. W. *J. Org. Chem.* **1978**, *43*, 3055. (e) Libermann, D. *Compt. Rend.* **1933**, *197*, 921. (f) Dougherty, G.; Hammond, P. D. *J. Am. Chem. Soc.* **1939**, *61*, 80. (g) Courtout, C.; Tung, T. Y. *Compt. Rend.* **1933**, *197*, 1227. (h) Kobayashi, M.; Minato, H.; Fukui, J.; Kamigata, N. *Bull. Chem. Soc. Jpn.* **1975**, *48*, 729. (i) Andersen, K. K.; Cinquini, M.; Papanikolaou, N. E. *J. Org. Chem.* **1970**, *35*, 706. (j) Andersen, K. K.; Caret, R. L.; Ladd, D. L. *J. Org. Chem.* **1976**, *41*, 3096.

(4) Andersen, K. K.; Papanikolaou, N. E. *Tetrahedron Lett.* **1966**, *45*, 5445.

(5) Miller, R. D.; Renaldo, A. F.; Ito, H. *J. Org. Chem.* **1988**, *53*, 5571.

(6) Osawa and co-workers of Shin-Etsu Co. Ltd. reported the synthesis of triarylsulfonium bromides using TMSCl and Grignard reagents. These studies were carried out independently. Refer to: (a) Osawa, Y.; Watanabe, S.; Okikawa, K.; Ishihara, T. *Chem. Abstr.* **1996**, *125*, 196653. (b) Osawa, Y.; Watanabe, S.; Kukemura, K.; Nakura, S.; Tanaka, H.; Kaai, Y. *Chem. Abstr.* **1998**, *128*, 121725.

(7) Refer to: (a) Oono, K.; Fukasawa, K.; Sakamoto, K.; Urano, F.; Sumino, M.; Imazeki, S. *Chem. Abstr.* **2001**, *135*, 76685. (b) Ishihara, M.; Sumino, M.; Fukasawa, K.; Maesawa, T.; Takano, N.; Imazeki, S. *Chem. Abstr.* **2002**, *136*, 217191. (c) Ishihara, M.; Sumino, M.; Fukasawa, K.; Maesawa, T.; Imazeki, S.; Sakuma, Y. *Chem. Abstr.* **2002**, *137*, 392177. (d) Ishihara, M.; Sumino, M.; Fukasawa, K.; Sakuma, Y. *Chem. Abstr.* **2002**, *137*, 302235.