# 1-Phenyl-1-benzothiophenium Triflates by a Direct S-Phenylation with Diphenyliodonium Triflate

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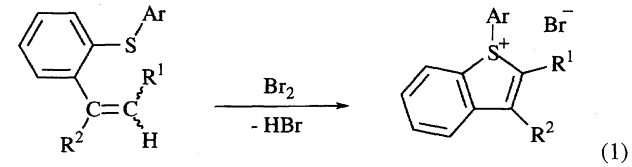
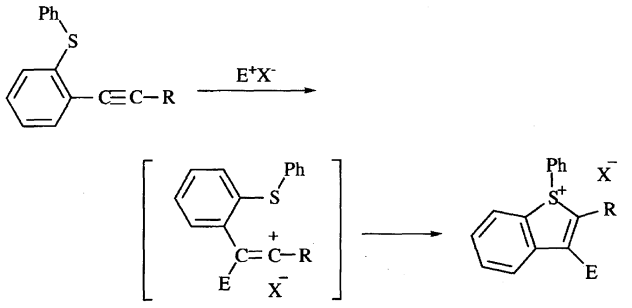
A parent 1-phenyl-1-benzothiophenium triflate was prepared by a direct phenylation of 1-benzothiophene with diphenyliodonium triflate in the presence of a catalytic amount of copper(II) acetate. Various substituted 1-phenyl-1-benzothiophenium triflates were successfully prepared by this method. The possible mechanism for the copper-catalyzed direct S-phenylation is discussed.

The chemistry of sulfonium salts has been recently developed in connection with the chemistry of hypervalent organosulfur compounds.[1] Also sulfonium salts have been applied as acid generators to photopolymerization processes and to chemical amplifications in imaging systems.[2] 1-Benzothiophenium salts are one of such sulfonium families and have an interesting heterocyclic sulfonium system. However, they have been rarely investigated before. The few examples are restricted to S-alkyl-substituted 1-benzothiophenium salts.[3] These S-alkyl-1-benzothiophenium salts have been prepared by alkylation of 1-benzothiophenes with alkyl halide in the presence of a silver salt or with a powerful alkylating agent.[4] Because of their instability they usually undergo dealkylation to return to the original 1-benzothiophenes. Therefore, a substituent forming a strong bond with sulfur atom is necessary for the purpose of investigating the chemical property of the benzothiophene ring. Generally, a phenyl group strengthens the chemical bond more than an alkyl group does. A Ph–S bond is about 12 kcal mol$^{-1}$ stronger than a Me–S bond.[5] For this purpose a phenyl group is suitable and we have started our work on the preparation of 1-phenyl-1-benzothiophenium salts.

Our previous works are related to intramolecular cyclization of vinyl cations bearing phenylsulfanyl group. In the course of the synthesis of the starting substrates, we have found that [2-(arylsulfanyl)phenyl]alkenes undergo intramolecular cyclization to give 1-aryl-1-benzothiophenium bromides during the bromination reaction (Eq. 1).[6] Also we have observed that the electrophilic addition of [2-(phenylsulfanyl)phenyl]alkynes affords 1-phenyl-1-benzothiophenium salts via intramolecular cyclization of the resulting vinyl cations (Eq. 2).[7] These intramolecular cyclizations leading to 1-benzothiophenium salts depend strongly on the nature of the cationic intermediates. The synthesis of 1-aryl-1-benzothiophenium salts by the above methods requires the substituent stabilizing the intermediates to cause the cyclization. Accordingly, these cyclization methods could not be applied to unsubstituted or less substituted S-aryl-1-benzothiophenium salts.




(1)




(2)

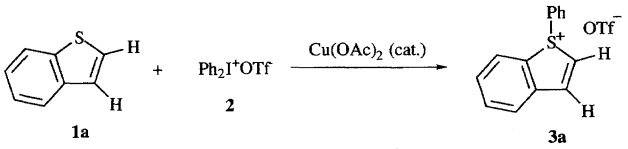
In the above electrophile-induced cyclization procedures, the preparations of *ortho*-substituted alkenes and alkynes are not simple and need several steps. The simple and useful procedure for the synthesis of 1-phenyl-1-benzothiophenium salts is a direct S-phenylation, in the same way as 1-alkyl-1-benzothiophenium salts have been prepared by the direct S-alkylation of 1-benzothiophenes. Benzenediazonium salts usually act as useful phenylating reagents, but the reaction of 1-benzothiophene using a benzenediazonium salt does not give the S-phenylation product.[8] Accordingly, other phenylating reagents have been required for the present purpose.

Diaryliodonium salts have been used effectively in arylation of nucleophilic substrates.[9] Especially, Crivello and Lam have prepared triarylsulfonium salts by arylation of diaryl sulfides.[10] This simple method has prompted us to apply arylation of 1-benzothiophenes as the method complementary to the electrophile-induced cyclizations. In the reaction

of 1-benzothiophene with diphenyliodonium triflate in the presence of a catalytic amount of copper(II) acetate, a fairy good yield of 1- phenyl-1-benzothiophenium triflate was obtained.[11] In this paper, we report a direct S-phenylation of 1-benzothiophenes using diphenyliodonium triflate and describe that this method is a widely utilizable one to solve the problems for the previous methods using the electrophile-induced cyclization.

## Results and Discussion

**Phenylation of 1-Benzothiophene (1a).** The phenylation reaction of 1-benzothiophenes (**1**) was conducted by use of diphenyliodonium triflate (**2**) and a catalytic amount of copper(II) acetate under nitrogen atmosphere. A mixture of 1-benzothiophene **1a**, diphenyliodonium triflate **2**, and a catalytic amount of $Cu(OAc)_2$ was heated at 140 °C for 30 min. The mixture turned dark brown within 5 min. Addition of ether to the reaction mixture and trituration gave crystals of 1-phenyl-1-benzothiophenium triflate (**3a**), which was isolated in 87% yield (Eq. 3). When the reaction was conducted for 60 min, the yield was 76%.




(3)

1-Phenyl-1-benzothiophenium triflate **3a** is quite stable and does not decompose up to the melting point (152 °C). It is also stable during chromatography on alumina or silica gel and does not change with any polar nucleophilic solvents, such as alcohols and DMSO.

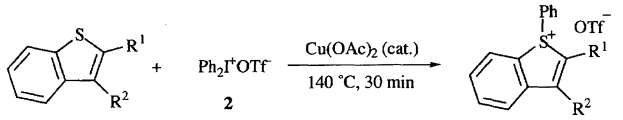
It is noteworthy that the phenylation of unsubstituted 1-benzothiophene proceeds very well to afford a high yield of 1-phenyl-1-benzothiophenium triflate **3a**. The parent 1-phenyl-1-benzothiophenium salt **3a** could not be prepared by the hitherto reported intramolecular cyclizations and was obtained for the first time by the present method. The structure of **3a** was fully characterized by $^1H$ and $^{13}C$ NMR, IR spectra and by combustion analysis. The characteristic down-field shift was observed in the protons at the 7 position and at the *ortho* position of the phenyl group. The crystal structure also was analyzed by a single crystal X-ray diffraction.[11]

**Other Examples.** The phenylation reaction was applied to the substituted 1-benzothiophenes **1** to study the scope and limitations of this procedure. The 1-benzothiophenes **1** bearing substituents such as methyl, phenyl, and 4-methoxyphenyl groups, were examined (Eq. 4). The results are given in Table 1. All the substituted and unsubstituted 1-benzothiophenes employed in this study undergo the S-phenylation in good to high yields. Occupation by two aryl groups at the 2 and 3 positions of 1-benzothiophene retards slightly the yield of S-phenylation products **3**. This may be attributed to the steric hindrance by two aryl groups.

Table 1. Preparation of 1-Phenyl-1-benzothiophenium Triflates **3**[a]

| Compound | $R^1$ | $R^2$ | Yield (%)[b] |
|---|---|---|---|
| **3a** | H | H | 83 |
| **3b** | Me | H | 94 |
| **3c** | H | Me | 81 |
| **3d** | Ph | H | 93 |
| **3e** | H | Ph | 70 |
| **3f** | Me | Ph | 94 |
| **3g** | Ph | Me | 88 |
| **3h** | Me | Me | 94 |
| **3i** | Ph | Ph | 69 |
| **3j** | *p*-$MeOC_6H_4$ | *p*-$MeOC_6H_4$ | 42 |

a) See experimental section for details. b) Isolated yields.

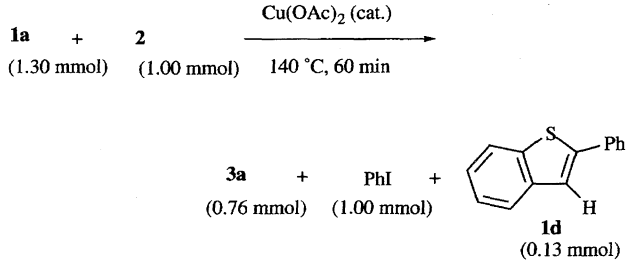



**1** **a:** $R^1 = R^2 = H$
**b:** $R^1$ = Me, $R^2$ = H
**c:** $R^1$ = H, $R^2$ = Me
**d:** $R^1$ = Ph, $R^2$ = H
**e:** $R^1$ = H, $R^2$ = Ph
**f:** $R^1$ = Me, $R^2$ = Ph
**g:** $R^1$ = Ph, $R^2$ = Me
**h:** $R^1$ = Me, $R^2$ = Me
**i:** $R^1 = R^2$ = Ph
**j:** $R^1 = R^2$ = 4-$MeOC_6H_4$

**3** **a:** $R^1 = R^2 = H$
**b:** $R^1$ = Me, $R^2$ = H
**c:** $R^1$ = H, $R^2$ = Me
**d:** $R^1$ = Ph, $R^2$ = H
**e:** $R^1$ = H, $R^2$ = Ph
**f:** $R^1$ = Me, $R^2$ = Ph
**g:** $R^1$ = Ph, $R^2$ = Me
**h:** $R^1$ = Me, $R^2$ = Me
**i:** $R^1 = R^2$ = Ph
**j:** $R^1 = R^2$ = 4-$MeOC_6H_4$

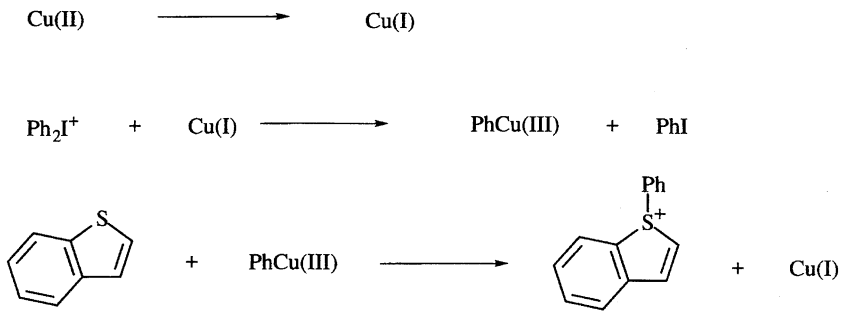
(4)

**Mechanistic Consideration.** The precise mechanism of the phenylation process catalyzed by a copper(II) salt has not been clearly understood. The reaction of 1-benzothiophene **1a** with diphenyliodonium triflate **2** provides some information for understanding the mechanism of the phenylation reaction. A gas chromatographic analysis of the ether-soluble by-products in the reaction at 140 °C for 60 min showed the existence of a quantitative amount of iodobenzene and a 13% yield of 2-phenyl-1-benzothiophene **1d** (Eq. 5).




(5)

The predominant formation of 2-phenyl-1-benzothiophene **1d** among the possible isomers and the absence of biphenyl are inconsistent with a mechanism in which a free phenyl radical plays an important role in the copper-catalyzed S-phenylation reaction. According to the reports by Beringer et al.[12] and by Caserio et al.,[13] both copper(I) and copper(II) species catalyze the decomposition of diaryliodonium salts. Lockhart demonstrated that copper(I) species are responsible




Scheme 1.

for the copper-catalyzed reaction of diaryliodonium salts.[14] Accordingly, it is considered that copper(I) species, in the present case, catalyze the phenylation of 1-benzothiophene **1a** as shown in Scheme 1. In this mechanism, a phenylcopper(III) intermediate[14] leads to the formation of 1-phenyl-1-benzothiophenium ion with regeneration of catalytically active Cu(I). In the process of the formation of 1-phenyl-1-benzothiophenium ion, 2-phenyl-1-benzothiophene **1d** is formed as the by-product. The possible generation of 2-phenyl-1-benzothiophene **1d** by the reaction of phenyl radical with the starting 1-benzothiophene is not in accord with the result of the present selective 2-phenylation, since homolytic substitution of 1-benzothiophene with phenyl radical takes place without selectivity.[15] The formation of the by-product may be attributed to the intervention of a phenylcopper(III) intermediate such as [PhCu(III)(**1a**)X]$^+$ or to the 1,5-phenyl shift and deprotonation of **3a**.

## Conclusion

1-Phenyl-1-benzothiophenium salts are very stable salts and applicable for investigation on the chemistry of 1-benzothiophenium ring. The use of unstable 1-alkyl-1-benzothiophenium salts is always in the danger of the dealkylation to the 1-benzothiophenes. Accordingly, 1-phenyl-1-benzothiophenium salts are the best candidates as the substrates suitable for investigation on the chemistry of 1-benzothiophenium ring. The preparations of the 1-aryl-1-benzothiophenium salts reported before require a multi-step synthesis involving a complex, intramolecular cyclization of *ortho*-arylsulfanyl substituted alkenes and -alkynes. We have found that the reaction of 1-benzothiophenes with diphenyliodonium triflate provides a direct synthesis of 1-phenyl-1-benzothiophenium triflates. The present method is a simple, wide-applicable procedure for various types of 1-aryl-1-benzothiophenium salts. This method will be useful for coming studies of 1-benzothiophenium chemistry.

## Experimental

**General.** Melting points were determined with a Yanaco melting point apparatus and are uncorrected. NMR spectra were taken with a Hitachi R 600, a Bruker AC-250, or a JEOL GSX 400 instrument. Gas chromatographic analysis was conducted by a Shimadzu GC-9A equipped with a glass column (2.0 m) packed with OV-17. Elemental analyses were performed by the Service Center of the Elementary Analysis of Organic Compounds, Faculty of Science, Kyushu University. 1-Benzothiophenes (**1a**) was purchased from Aldrich Chemical Co. Substituted 1-benzothiophenes (**1b—j**) were prepared according to the following references: **1b**,[16] **1c**,[17] **1d**,[18] **1e**,[19] **1f**,[20] **1g**,[21] **1h**,[17] **1i**,[22] and **1j**.[23] Diphenyliodonium triflate (**2**) was prepared by our method.[24]

**General Procedure for Preparation of 1-Phenyl-1-benzothiophenium Triflates (3).** A mixture of a 1-benzothiophene (**1**) (1.0 mmol), diphenyliodonium triflate (**2**) (1.3 mmol) and copper-(II) acetate (0.01 mmol) was heated with stirring at 140 °C for 30 min under $N_2$ atmosphere. The reaction mixture was cooled to room temperature and ether was added. The resulting crystals were triturated, collected by filtration, and washed with ether to remove iodobenzene and the by-products. The collected crystals were dried in vacuo and identified as 1-phenyl-1-benzothiophenium triflates (**3**) on the basis of the spectral data and the combustion analysis. Further purification for the combustion analysis was conducted by recrystallization from a mixture of $CH_2Cl_2$ and $CCl_4$.

**1-Phenyl-1-benzothiophenium Triflate (3a):** Mp 152—153 °C; $^1$H NMR (DMSO-$d_6$) $\delta$=7.61—7.80 (m, ArH, 7H), 7.87 (t, $J$=8 Hz, ArH, 1H), 8.09 (d, $J$=8 Hz, ArH, 1H), 8.26 (d, $J$=6 Hz, ArH, 1H); $^{13}$C NMR (DMSO-$d_6$) $\delta$=124.88, 126.41, 127.28, 127.50, 129.93, 130.66, 131.10, 133.31, 134.07, 135.55, 140.92, 142.51; IR (KBr) 1270, 1225, 1155 cm$^{-1}$ (OTf). Found: C, 49.86; H, 3.03%. Calcd for $C_{15}H_{11}F_3O_3S_2$: C, 50.00; H, 3.08%.

**2-Methyl-1-phenyl-1-benzothiophenium Triflate (3b):** Mp 168—169 °C; $^1$H NMR (DMSO-$d_6$) $\delta$=2.38 (s, Me, 3H), 7.65—7.90 (m, ArH, 8H), 8.01 (d, $J$=8 Hz, ArH, 1H), 8.31 (d, $J$=8 Hz, ArH, 1H); $^{13}$C NMR (DMSO-$d_6$) $\delta$=13.57, 123.81, 126.48, 127.86, 129.70, 130.32, 131.51, 133.76, 134.21, 134.61, 136.18, 140.27, 142.51. Found: C, 51.33; H, 3.52%. Calcd for $C_{16}H_{13}F_3O_3S_2$: C, 51.33; H, 3.50%.

**3-Methyl-1-phenyl-1-benzothiophenium Triflate (3c):** Mp 143—144 °C; $^1$H NMR (DMSO-$d_6$) $\delta$=2.61 (d, $J$=1 Hz, Me, 3H), 7.50 (d, $J$=1 Hz, ArH, 1H), 7.62—7.77 (m, ArH, 6H), 7.91 (t, $J$=8 Hz, ArH, 1H), 8.05 (d, $J$=8 Hz, ArH, 1H), 8.25 (d, $J$=8 Hz, ArH, 1H); $^{13}$C NMR (DMSO-$d_6$) $\delta$=14.46, 118.55, 125.52, 125.86, 127.05, 129.88, 130.72, 131.06, 133.20, 134.02, 135.72, 141.34, 153.44. Found: C, 51.25; H, 3.52%. Calcd for $C_{16}H_{13}F_3O_3S_2$: C, 51.33; H, 3.50%.

**1,2-Diphenyl-1-benzothiophenium Triflate (3d):** Mp 175—177 °C; $^1$H NMR (DMSO-$d_6$) $\delta$=7.44—7.79 (m, ArH, 12H), 8.13 (d, $J$=8 Hz, ArH, 1H), 8.41 (d, $J$=8 Hz, ArH, 1H), 8.58 (s, ArH, 1H); $^{13}$C NMR (DMSO-$d_6$) $\delta$=124.36, 127.35, 127.41, 127.59, 127.74, 129.64, 130.50, 130.77, 131.44, 133.77, 134.03, 134.58, 134.71, 142.50, 142.67 (one signal is overlapped). Found: C, 58.00; H, 3.48%. Calcd for $C_{21}H_{15}F_3O_3S_2$: C, 57.79; H, 3.46%.

**1,3-Diphenyl-1-benzothiophenium Triflate (3e):** Mp 168—169 °C; $^1$H NMR (DMSO-$d_6$) $\delta$=7.65—8.36 (m, ArH, 15H); $^{13}$C NMR (DMSO-$d_6$) $\delta$=119.99, 126.55, 127.83, 128.62, 129.24, 130.13, 130.78, 130.87, 130.91, 131.18, 133.30, 134.14, 136.43, 139.68, 154.26 (one peak is overlapped). Found: C, 57.52; H,

3.45%. Calcd for $C_{21}H_{15}F_3O_3S_2$: C, 57.79; H, 3.46%.

**2-Methyl-1,3-diphenyl-1-benzothiophenium Triflate (3f):** Amorphous solid; $^1$H NMR (DMSO-$d_6$) $\delta$=2.32 (s, Me, 3H), 7.59—8.37 (m, ArH, 14H). 1-Benzothiophenium triflate **3f** could not be purified because of its hygroscopic property and some impurity. Accordingly, **3f** was confirmed by conversion to the known perchlorate[6b] with an excess amount of $LiClO_4$: $^1$H NMR ($CDCl_3$) $\delta$=2.33 (s, Me, 3H), 7.50—7.79 (m, ArH, 13H), 8.15 (d, $J$=8 Hz, ArH, 1H).

**3-Methyl-1,2-diphenyl-1-benzothiophenium Triflate (3g):** Mp 158—162 °C; $^1$H NMR (DMSO-$d_6$) $\delta$=2.61 (s, Me, 3H), 7.44—7.82 (m, ArH, 11H), 8.01 (t, $J$=8 Hz, ArH, 1H), 8.18 (d, $J$=8 Hz, ArH, 1H), 8.40 (d, $J$=8 Hz, ArH, 1H); $^{13}$C NMR (DMSO-$d_6$) $\delta$=13.56, 124.19, 126.07, 127.37, 127.43, 129.38, 129.99, 130.31, 130.63, 131.30, 133.57, 133.94, 134.33, 134.67, 143.88, 144.53 (one peak is overlapped). Found: C, 58.46; H, 3.82%. Calcd for $C_{22}H_{17}F_3O_3S_2$: C, 58.67; H, 3.81%.

**2,3-Dimethyl-1-phenyl-1-benzothiophenium Triflate (3h):** Mp 111—112 °C; $^1$H NMR (DMSO-$d_6$) $\delta$=2.32 (s, Me, 3H), 2.46 (s, Me, 3H), 7.61—8.03 (m, ArH, 8H), 8.22—8.30 (m, ArH, 1H); $^{13}$C NMR (DMSO-$d_6$) $\delta$=11.33, 12.34, 1224.20, 124.98, 127.35, 129.89, 130.44, 131.42, 132.80, 133.66, 134.58, 143.42, 144.77. Found: C, 52.39; H, 3.91%. Calcd for $C_{17}H_{15}F_3O_3S_2$: C, 52.57; H, 3.89%.

**1,2,3-Triphenyl-1-benzothiophenium Triflate (3i):** Mp 163—164 °C; $^1$H NMR (DMSO-$d_6$) $\delta$=7.26—7.31 (m, ArH, 5H), 7.49—7.85 (m, ArH, 13H), 8.35 (d, $J$=9 Hz, ArH, 1H); $^{13}$C NMR ($CDCl_3$) $\delta$=122.70, 126.62, 127.04, 128.68, 129.07, 129.38, 129.62, 129.86, 130.12, 130.36, 130.57, 130.66, 131.07, 131.66, 132.20, 134.12, 135.10, 135.95, 143.09, 146.51. Found: C, 63.09; H, 3.78%. Calcd for $C_{27}H_{19}F_3O_3S_2$: C, 63.27; H, 3.74%.

**2,3-Bis(4-methoxyphenyl)-1-phenyl-1-benzothiophenium Triflate (3j):** Mp 139—140 °C; $^1$H NMR (DMSO-$d_6$) $\delta$=3.73 (s, OMe, 3H), 3.89 (s, OMe, 3H), 6.76 (d, $J$=8 Hz, ArH, 2H), 7.06 (d, $J$=8 Hz, ArH, 2H), 7.23—7.80 (m, ArH, 14H), 8.27 (d, $J$=8 Hz, ArH, 1H); $^{13}$C NMR (DMSO-$d_6$) $\delta$=55.10, 55.39, 114.79, 114.97, 115.12, 118.89, 122.11, 123.17, 130.50, 130.68, 131.44, 131.57, 131.82, 135.00, 143.35, 144.28, 160.90, 161.00. Found: C, 60.57; H, 4.05%. Calcd for $C_{29}H_{23}F_3O_3S_2$: C, 60.83; H, 4.05%.

**Analysis of the By-products from the Reaction of 1-Benzothiophene (1a) and Diphenyliodonium Triflate (2).** A mixture of **1a** (1.30 mmol), **2** (1.00 mmol), and $Cu(OAc)_2$ (10 mg) was heated as described in the general procedure. After filtration of crystalline 1-phenyl-1-benzothiophenium triflate (**3a**), the filtrate was analyzed by GC using a glass column packed with 5% OV-17 on Chromosorb W (2.0 m×2.6 mm). The by-products were identified by the retention time compared with the authentic samples. The chromatogram showed the formation of iodobenzene (1.00 mmol), 1-benzothiophene **1a** (0.29 mmol) and 2-phenyl-1-benzothiophene **1d** (0.13 mmol). 2-Phenyl-1-benzothiophene **1d** was further isolated by column chromatography on alumina with hexane–$CH_2Cl_2$ eluants, mp 171—176 °C (lit,[18] 174—175 °C).

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