

Novel [4 + 2]-Cycloaddition of 1-Phenyl-1-benzothiophenium Salts with Dienes. Experimental Evidence for a Lack of Aromaticity in the Thiophene Ring

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Received June 13, 2002

The [4 + 2]-cycloaddition reaction of 1-phenyl-1-benzothiophenium triflates has been conducted for the first time. [4 + 2]-Cycloaddition with dienes such as cyclopentadiene and 1,3-diphenylisobenzofuran occurs successfully to give cycloadducts. This result indicates that the C=C bond of the thiophene ring acts as a 2π electron component in the cycloaddition reaction. Cycloadducts were formed in high yields with high stereoselectivity. However, the cycloaddition with other less reactive dienes such as 2,3-dimethyl-1,3-butadiene did not take place. The structure and stereochemistry of cycloadduct **2a** were analyzed by NMR techniques. Furthermore, reaction of the cycloadducts with sodium methoxide in methanol gave the ring-opened products in high yields.

Introduction

The [4 + 2]-cycloaddition reaction (the Diels–Alder reaction) is a standard method for preparing six-membered ring systems that are versatile building blocks for synthesis of numerous natural and nonnatural cyclic compounds.¹ In particular, this [4 + 2] process enables the synthesis of biologically important nitrogen-, sulfur-, and oxygen-containing heterocycles that have been hitherto inaccessible or difficult to prepare by standard methods.² Aromatic heterocyclic compounds can be used for accomplishing some synthetic transformations,³ but they have low reactivity in general due to the aromatic character of heterocycles, especially thiophene and benzothiophene,⁴ which do not readily undergo cycloaddition

reactions under ordinary conditions. However, when thiophenes are transformed into the corresponding *S*-oxides, the aromaticity of the thiophene ring is destroyed. In fact, thiophene monoxides formed by oxidation of thiophenes successfully undergo the Diels–Alder cycloaddition as a diene component.⁵

On the other hand, 1-benzothiophenes are of interest in many pharmaceutical fields, since they exhibit a variety of biological properties, such as antiallergic and ocular hypotensive activities.⁶ However, the corresponding onium-type benzothiophenes, 1-benzothiophenium salts, have been little investigated so far. Although 1-alkyl-1-benzothiophenium salts have been prepared, these salts are lacking in stability to be tolerant to the usual reaction conditions.⁷

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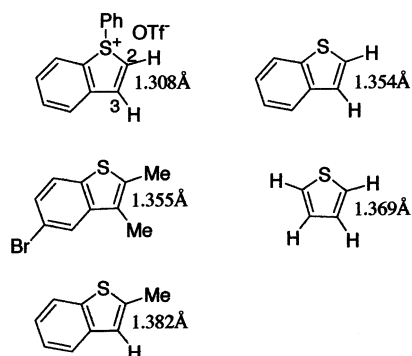
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CHART 1



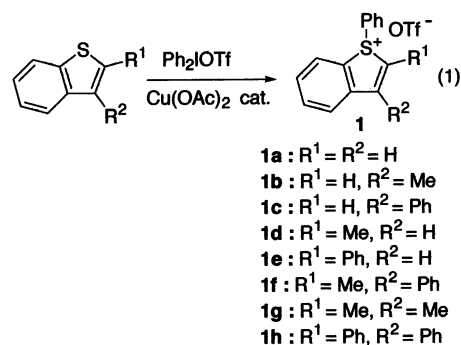
Recently, we reported several methods for the preparation of a wide variety of 1-phenyl-1-benzothiophenium salts and demonstrated the stability of the sulfonium moiety sufficiently to investigate the chemistry of 1-benzothiophenium ion.^{8,9} The triflate salt of 1-phenyl-1-benzothiophenium ion shows the tetrahedral structure around the sulfur atom with the phenyl group being out of the plane and the large bond alternation.^{8e} The short C(2)–C(3) bond length of 1.308 Å is much shorter than the corresponding values of 1-benzothiophene (1.354 Å, calculated value),¹⁰ 5-bromo-2,3-dimethyl-1-benzothiophene (1.355 Å),¹¹ thiophene (1.369 Å)¹² and 2-methyl-1-benzothiophene (1.382 Å).¹³

This structural outcome suggests the lack of aromaticity of the thiophene ring in the 1-phenyl-1-benzothiophenium ion. Consequently, it is expected that the C(2)–C(3) bond shows an olefinic nature and behaves as the dienophile in [4 + 2]-cycloaddition reactions. There are a few reports on the theoretical study of thiophenium salts,^{4b,c,14} demonstrating that the aromaticity of the thiophene ring is destroyed. However, there is no experimental evidence for the lack of aromaticity. Thus, we have examined the [4 + 2]-cycloaddition of 1-phenyl-1-benzothiophenium triflates with dienes.¹⁵ Here we report our findings that 1-phenyl-1-benzothiophenium ions un-

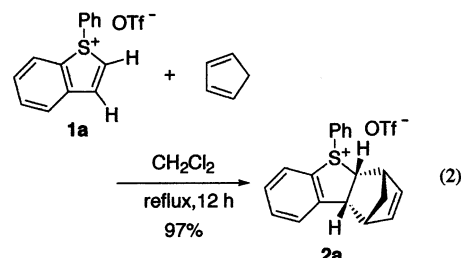
dergo cycloaddition to give the corresponding cycloadducts with dienes. We also describe the structural determination and chemical stability of the cycloadducts.

Results and Discussion

Cycloaddition of 1-Phenyl-1-benzothiophenium Triflate (1a) with Cyclopentadiene. 1-Phenyl-1-benzothiophenium triflates **1** were prepared in high yields by the reaction of 1-benzothiophenes with diphenyliodonium triflate in the presence of a catalytic amount of copper(II) acetate at 140°C (eq 1).^{8f}



When the reaction of 1-phenyl-1-benzothiophenium triflate **1a** with cyclopentadiene (5 equiv) was carried out in CH₂Cl₂ at the refluxing temperature for 12 h, crystalline adduct **2a** was obtained in 97% yield (eq 2). The polycyclic structure and stereochemistry of cycloadduct **2a** were established by NMR techniques. The spectra and elemental analysis indicated either isomer of possible endo and exo adducts.



The ¹³C NMR spectrum of **2a** exhibited the signals of 17 carbon atoms, and the DEPT experiments showed 14 protonated carbon signals, thereby revealing that there are three quaternary carbons in the molecule. The DEPT-135 spectrum showed 13 positive signals due to CH and one negative signal due to a CH₂ carbon; the presence of two benzene rings was observed from the 10 positive signals at δ 127.0–147.8. The ¹H NMR spectrum of **2a** showed two olefinic protons at δ = 5.77 (dd, *J* = 2.7, 5.4 Hz, 1H) and 6.43 (dd, *J* = 2.7, 5.4 Hz, 1H) and six aliphatic protons at δ = 1.87 (s, 2H), 3.56 (s, 1H), 3.93 (s, 1H), 4.98 (dd, *J* = 3.9, 7.6 Hz, 1H), and 5.12 (dd, *J* = 3.9, 7.6 Hz, 1H), along with aromatic protons at δ 7.48–7.74 (m, 9H).

The heteronuclear ¹H/¹³C correlation led to the assignment of all protons and carbons as shown in Figure 1.

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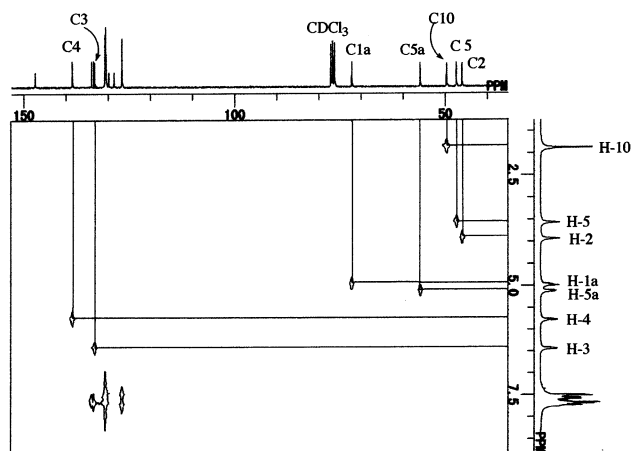


FIGURE 1. Contour plot of ^1H - ^{13}C shift correlation for **2a**.

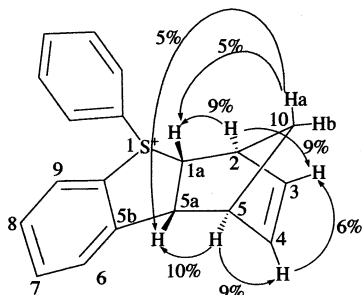


FIGURE 2. NOE relations in **2a**.

All aliphatic carbons of **2a** bound with protons were assigned from the cross-peak. The large chemical shifts observed for the alkyl protons H-1a and H-5a are attributed to a shielding effect by the benzene ring.

The stereochemistry of **2a** was determined by NOE experiments (Figure 2). The irradiation of proton H-10 showed the enhancement (5% each) of the signals of protons H-1a and H-5a, indicating that they are spatially close one another. The observed vicinal proton coupling constants ($J_{3,4} = 5.4$ Hz, $J_{2,3} = J_{4,5} = 2.7$ Hz, $J_{1a,2} = J_{5,5a} = 3.9$ Hz, and $J_{1a,5a} = 7.6$ Hz) also fall into the characteristic ranges of the norbornene structure.¹⁵ Accordingly, adduct **2a** is considered to be the endo adduct. The assignment of the structure of **2a** gave good agreement with the results of the single-crystal X-ray structural analysis.¹⁶ The formation of cycloadduct **2a** experimentally indicates that the aromaticity of the thiophene ring is destroyed and the C2–C3 bond has an olefinic character.

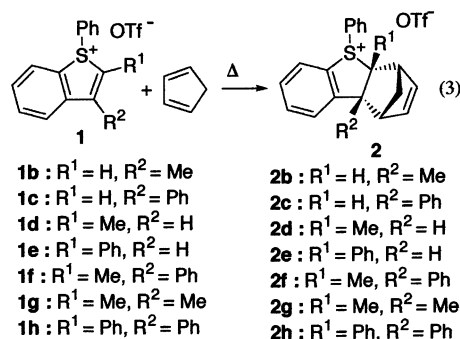
Cycloaddition of Other 1-Phenyl-1-benzothiophenium Triflates **1 with Cyclopentadiene.** To examine the scope and limitations of this cycloaddition, we conducted the reaction of substituted 1-phenyl-1-benzothiophenium triflates (**1b–h**) with cyclopentadiene (eq 3). The results are summarized in Table 1. When the reaction of 3-methyl-1-phenyl-1-benzothiophenium triflate (**1b**) with cyclopentadiene was carried out in a refluxing solution of CH_2Cl_2 or at 45 °C in MeCN, no cycloadduct **2b** was obtained at all (entries 1 and 2). However, when the reaction of **1b** with cyclopentadiene

TABLE 1. Cycloaddition of **1** with Cyclopentadiene

entry	1	solvent	temp (°C)	time (h)	product	yield (%)
1	1b	CH_2Cl_2	reflux	12	2b	0
2	1b	MeCN	45	72	2b	0
3	1b	MeCN	50 ^a	72	2b	22
4	1b	MeCN	60 ^a	72	2b	74
5	1c	MeCN	45	72	2c	25
6	1c	MeCN	50 ^a	72	2c	68
7	1c	MeCN	60 ^a	72	2c	80
8	1d	MeCN	60 ^a	72	2d	73

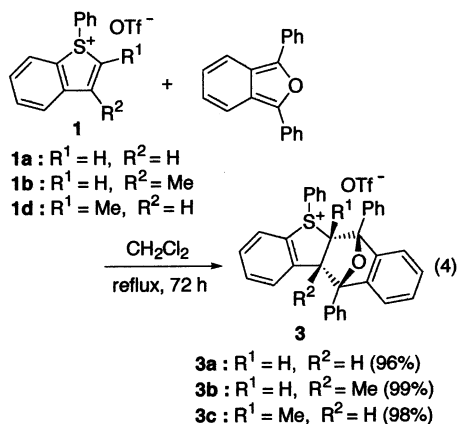
^a In a sealed tube.

was carried out in a sealed tube at 50 °C for 72 h, cycloadduct **2b** was obtained in 22% yield (entry 3). In the case of 1,3-diphenyl-1-benzothiophenium triflate (**1c**), the reaction of **1c** with cyclopentadiene at 45 °C in MeCN gave cycloadduct **2c** in 25% yield and the same reaction in a sealed tube at 50 °C afforded a better yield (68%) of **2c** (entries 5 and 6). The best result (80% yield of **2c**) was obtained in the reaction in a sealed tube at 60 °C for 72 h (entry 7). Further, when reactions of **1b** and **1d** were conducted in a sealed tube at 60 °C for 72 h, cycloadducts **2b** and **2d** were obtained in 74 and 73% yields, respectively (entries 4 and 8). On the other hand, 1,2-diphenyl-1-benzothiophenium (**1e**), 2-methyl-1,3-diphenyl-1-benzothiophenium (**1f**), 2, 3-dimethyl-1-phenyl-1-benzothiophenium (**1g**), and 1,2,3-triphenyl-1-benzothiophenium (**1h**) triflates did not undergo cycloaddition with cyclopentadiene under any of the above conditions. Therefore, it is considered that the presence of the substituent at the 2- or 3-position, especially the 2-position, has a strong influence on the cycloaddition of 1-phenyl-1-benzothiophenium salts **1**. The strong retardation of the reaction by the substituent at the 2-position is mainly attributed to steric repulsion with a phenyl group.



Although other dienes such as 2,3-dimethyl-1,3-butadiene and 1,3-diphenylisobenzofuran were examined in the cycloaddition reaction, only 1,3-diphenylisobenzofuran underwent cycloaddition with 1-phenyl-1-benzothiophenium salts **1**. When the reaction of 1-phenyl-1-benzothiophenium triflate **1a** with 1,3-diphenylisobenzofuran was carried out in CH_2Cl_2 at the refluxing temperature, cycloadduct **3a** was obtained in 96% yield (eq 4). Similarly, the reaction of benzothiophenium triflates **1b** and **1d** with 1,3-diphenylisobenzofuran afforded the corresponding cycloadducts **3b** and **3c** in 99 and 95% yields, respectively. However, benzothiophenium triflates **1c**, **1e**, and **1g** failed to undergo cycloaddition under the same reaction conditions.

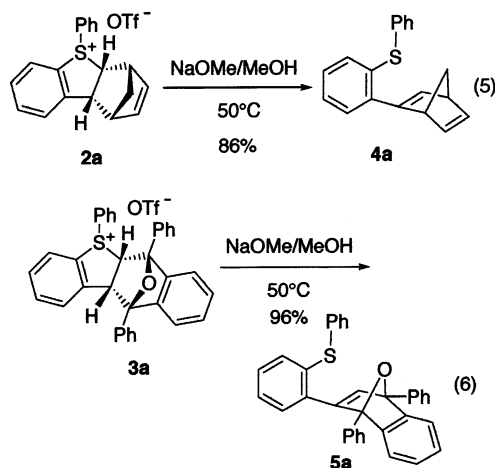
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Reactivity of Cycloadducts 2 and 3 with Sodium Methoxide. Sulfonium salts are known to undergo substitutions, eliminations, and ylide formation and rearrangements.¹⁷ Cyclic sulfonium salts also react with many reagents, mostly nucleophiles.¹⁸ Because 1-alkyl-1-benzothiophenium salts are much higher in chemical reactivity than the corresponding 1-phenyl-1-benzothiophenium salts,¹⁹ the cycloadducts, 1-phenyl-2,3-dihydro-1-benzothiophenium salts, are expected to be more reactive. Previously, we reported that 1-aryl-1-benzothiophenium salts undergo the ring-opening reaction upon treatment with methoxide anion.²⁰ To compare the reactivity of the cycloadducts with that of 1-phenyl-1-benzothiophenium salts, we examined the reaction of the cycloadducts with sodium methoxide in methanol. The cycloadducts were quite stable in the presence of hydroxide and methoxide anions at room temperature. When cycloadduct **2a** reacted with sodium methoxide in methanol at 50 °C for 12 h, the ring-opening product (**4a**) was obtained in 86% yield (eq 5). Similarly, when cycloadduct **3a** reacted under the same reaction conditions, the ring-opened product (**5a**) was formed in 96% yield (eq 6). However, the phenyl-substituted cycloadduct **2c** did not react under the same conditions and was recovered without change. Compared with 1-phenyl-1-benzothiophenium salts, cycloadducts **2** and **3** are more stable toward methoxide ion, although the thiophene ring is partly saturated. It is considered that this low reactivity is attributed to the steric congestion around the reaction center. Especially, in cycloadduct **2c**, the polycyclic structure completely blocked the saturated sp³ carbon bound to sulfur against attack by reagents.

Conclusion

We have found a novel [4 + 2]-cycloaddition reaction of 1-phenyl-1-benzothiophenium salts with cyclopentadiene or 1,3-diphenylisobenzofuran and experimentally



confirmed the olefinic nature of the thiophene ring arising from a lack of aromaticity. The transformation of benzothiophene into the *S*-phenylbenzothiophenium ion is an excellent method for [4 + 2]-cycloaddition. Further applications including thiophenes are now in progress.

Experimental Section

Cycloaddition of 1-Phenyl-1-benzothiophenium Triflate 1a with Cyclopentadiene. To a solution of 1-phenyl-1-benzothiophenium triflate **1a** (0.65 g, 2.0 mmol) in CH₂Cl₂ (10 mL) was added cyclopentadiene (0.66 g, 10 mmol), and the reaction mixture was refluxed with stirring for 12 h. The solvent was then evaporated under reduced pressure, and the resulting crystals were purified by recrystallization from Et₂O–CH₂Cl₂ to give 1.66 g (97%) of *cis*-1a-*transoid*-1a,2-*cis*-2-1a,2,5,5a-tetrahydro-2,5-methano-1-phenyldibenzothiophenium triflate (**2a**) as colorless crystals: mp 147.1–147.2 °C; ¹H NMR (CDCl₃) δ 1.87 (s, 2H, CH₂), 3.56 (s, 1H, CH), 3.93 (s, 1H, CH), 4.98 (dd, *J* = 3.9, 7.6 Hz, 1H, CH), 5.12 (dd, *J* = 3.9, 7.6 Hz, 1H, CH), 5.77 (dd, *J* = 2.7, 5.4 Hz, 1H, CH), 6.43 (dd, *J* = 2.7, 5.4 Hz, 1H, CH), 7.48–7.74 (m, 9H, ArH); ¹³C NMR (CDCl₃) δ 46.6, 47.9, 50.2, 56.6, 72.9, 127.0, 127.1, 129.0, 130.5, 130.9, 131.1, 131.2, 133.79, 133.84, 134.4, 138.7, 147.8. Anal. Calcd for C₂₀H₁₇F₃O₃S₂: C, 56.33; H, 4.02. Found: C, 56.36; H, 4.02.

Cycloaddition of Other 1-Phenyl-1-benzothiophenium Triflate 1 with Cyclopentadiene. A glass tube was charged with 1-phenyl-1-benzothiophenium triflate **1** (1 mmol), cyclopentadiene (5 mmol), and MeCN (2–3 mL). The glass tube was placed in a 20 mL stainless steel autoclave. The autoclave was closed and gradually heated to 60 °C. The temperature was kept for 72 h. After cooling to room temperature, the autoclave was opened. The solvents were evaporated, and the product was purified by recrystallization from Et₂O–CH₂Cl₂ to give the following cycloadducts **2** as crystals.

1a,2,5,5a-Tetrahydro-2,5-methano-5a-methyl-1-phenyldibenzothiophenium Triflate (2b): yield, 75%; mp 133–134 °C; ¹H NMR (CDCl₃) δ 1.92 (s, 3H, CH₃), 1.96 (d, *J* = 9.9 Hz, 1H, CH), 2.04 (d, *J* = 9.9 Hz, 1H, CH), 3.17 (s, 1H, CH), 4.13 (s, 1H, CH), 4.48 (d, *J* = 3.9 Hz, 1H, CH), 5.74 (dd, *J* = 3.0, 5.4 Hz, 1H, CH), 6.41 (dd, *J* = 3.0, 5.4 Hz, 1H, CH), 7.51–7.76 (m, 9H, ArH); ¹³C NMR (CDCl₃) δ 28.3, 47.4, 48.7, 54.2, 63.7, 78.4, 125.9, 127.5, 128.5, 128.9, 130.7, 130.9, 131.2, 132.7, 134.1, 134.2, 140.4, 152.6. Anal. Calcd for C₂₁H₁₉F₃O₃S₂: C, 57.26; H, 4.35. Found: C, 57.22; H, 4.31.

1a,2,5,5a-Tetrahydro-2,5-methano-1,5a-diphenyldibenzothiophenium Triflate (2c): yield, 82%; mp 84–87 °C; ¹H NMR (CDCl₃) δ 1.81 (d, *J* = 9.6 Hz, 1H, CH), 1.98 (d, *J* = 9.6 Hz, 1H, CH), 4.02 (s, 1H, CH), 4.36 (s, 1H, CH), 5.03 (d, *J* = 4.5 Hz, 1H, ArH), 5.82 (dd, *J* = 3.3, 5.4 Hz, 1H, CH), 6.72 (dd, *J* = 3.3, 5.4 Hz, 1H, CH), 7.20–7.32 (m, 5H, ArH), 7.41 (d,

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$J = 7.8$ Hz, 1H, ArH), 7.58–7.72 (m, 8H, ArH); ^{13}C NMR (CDCl_3) δ 47.8, 49.2, 52.8, 72.6, 79.6, 125.3, 127.0, 127.6, 128.0, 128.3, 128.4, 129.5, 130.2, 130.8, 131.1, 134.2, 134.3, 135.8, 139.3, 141.5, 152.8. Anal. Calcd for $\text{C}_{26}\text{H}_{21}\text{F}_3\text{O}_3\text{S}_2$: C, 62.13; H, 4.21. Found: C, 62.04; H, 4.20.

1a,2,5,5a-Tetrahydro-2,5-methano-1a-methyl-1-phenyldibenzothiophenium Triflate (2d): yield, 73%; mp 118–119 °C; ^1H NMR (CDCl_3) δ 1.49 (s, 3H, CH_3), 2.01–2.03 (m, 2H, CH_2), 3.42 (brs, 1H, CH), 3.79 (brs, 1H, CH), 4.32 (d, $J = 4.2$ Hz, 1H, CH), 5.79 (dd, $J = 3.0, 5.4$ Hz, 1H, CH), 6.73 (dd, $J = 3.0, 5.4$ Hz, 1H, CH), 7.35–7.73 (m, 9H, ArH); ^{13}C NMR (CDCl_3) δ 24.2, 48.6, 49.7, 53.4, 63.7, 85.2, 125.4, 125.6, 127.02, 127.03, 127.2, 127.8, 130.9, 133.8, 134.6, 136.5, 138.7, 148.6. Anal. Calcd for $\text{C}_{21}\text{H}_{19}\text{F}_3\text{O}_3\text{S}_2$: C, 57.26; H, 4.35. Found: C, 57.19; H, 4.36.

Cycloaddition of 1-Phenyl-1-benzothiophenium Triflate 1 with 1,3-Diphenylisobenzofuran. 1a,2,7,7a-Tetrahydro-2,7-epoxy-1,2,7-triphenylbenzonaphthothiophenium Triflate (3a). A mixture of 1-phenyl-1-benzothiophenium triflate **1a** (0.74 g, 2 mmol) and 1,3-diphenylisobenzofuran (1.08 g, 4 mmol) in CH_2Cl_2 (12 mL) was refluxed with stirring for 72 h. The solvent was evaporated under reduced pressure, and the resulting crystals were purified by recrystallization from Et_2O –acetone to give adduct **3a** (1.19 g, 96%) as white crystals: mp 165–166 °C; ^1H NMR (CDCl_3) δ 5.19 (d, $J = 8.4$ Hz, 1H, CH), 6.28 (d, $J = 8.4$ Hz, 1H, CH), 6.59 (d, $J = 7.2$, 1H, ArH), 6.99 (t, $J = 7.2$ Hz, 1H, ArH), 7.24–8.00 (m, 21H, ArH); ^{13}C NMR (CDCl_3) δ 59.7, 74.0, 89.9, 93.6, 122.0, 122.5, 125.9, 126.8, 127.8, 128.5, 128.6, 129.07, 129.13, 129.2, 129.3, 129.4, 129.7, 130.2, 130.8, 131.5, 131.7, 133.1, 134.1, 134.2, 134.9, 141.0, 143.8, 144.9. Anal. Calcd for $\text{C}_{35}\text{H}_{25}\text{F}_3\text{O}_4\text{S}_2$: C, 66.65; H, 4.00. Found: C, 66.58; H, 4.26.

1a,2,7,7a-Tetrahydro-2,7-epoxy-7a-methyl-1,2,7-triphenylbenzonaphthothiophenium Triflate (3b). A mixture of 3-methyl-1-phenyl-1-benzothiophenium triflate **1b** (0.33 g, 1 mmol) and 1,3-diphenylisobenzofuran (0.54 g, 2 mmol) in CH_2Cl_2 (5 mL) was refluxed with stirring for 72 h: yield, 0.64 g, 99%; mp 159–162 °C; ^1H NMR (CDCl_3) δ 1.67 (s, 3H, CH_3), 5.42 (s, 1H, CH), 6.66 (d, $J = 8.4$ Hz, 1H, ArH), 7.19–7.47 (m, 11H, ArH), 7.58–7.82 (m, 11H, ArH); ^{13}C NMR (CDCl_3) δ 26.3, 69.7, 85.7, 90.4, 94.6, 120.5, 121.6, 122.3, 125.2, 125.9, 126.3, 126.4, 126.9, 127.9, 128.79, 128.83, 129.7, 129.8, 130.3, 131.3, 131.8, 131.9, 133.0, 134.1, 135.3, 135.9, 142.2, 143.6, 149.1. Anal. Calcd for $\text{C}_{36}\text{H}_{27}\text{F}_3\text{O}_4\text{S}_2$: C, 67.07; H, 4.22. Found: C, 66.79; H, 4.19.

1a,2,7,7a-Tetrahydro-2,7-epoxy-1a-methyl-1,2,7-triphenylbenzonaphthothiophenium Triflate (3c). A mixture of 2-methyl-1-phenyl-1-benzothiophenium triflate **1d** (0.37 g, 1 mmol) and 1,3-diphenylisobenzofuran (0.54 g, 2 mmol) in CH_2Cl_2 (5 mL) was refluxed with stirring for 72 h: yield, 0.63 g, 98%; mp 145–146 °C; ^1H NMR (CDCl_3) δ 1.22 (s, 3H, CH_3), 5.48 (s, 1H, CH), 6.49 (d, $J = 7.2$ Hz, 1H, ArH), 6.97 (t, $J = 7.2$ Hz, 1H, ArH), 7.26–7.96 (m, 22H, ArH); ^{13}C NMR (CDCl_3) δ 22.3, 66.1, 81.9, 92.1, 93.2, 121.7, 123.1, 124.5, 125.1, 126.7, 127.4, 128.26, 128.27, 128.5, 129.0, 129.1, 129.3, 129.5, 130.2, 131.2, 131.3, 133.2, 133.4, 134.01, 134.02, 140.0, 140.5, 144.7, 145.9. Anal. Calcd for $\text{C}_{36}\text{H}_{27}\text{F}_3\text{O}_4\text{S}_2$: C, 67.07; H, 4.22. Found: C, 66.96; H, 4.48.

Reaction of Cycloadducts 2 and 3 with Sodium Methoxide. 2-[2-(Phenylthio)phenyl]bicyclo[2.2.1]hept-2,5-diene (4a). A mixture of **2a** (0.34 g, 0.8 mmol), sodium methoxide (0.13 g, 2.4 mmol), and methanol (5 mL) was heated for 12 h at 50 °C. The reaction mixture was cooled to room temperature and extracted with Et_2O (3×b025 mL). The combined ethereal extract was dried over anhydrous sodium sulfate. The solvent was removed, and the residue was separated by column chromatography on alumina using CH_2Cl_2 as an eluent to yield **4a** (0.19 g, 86%) as a white solid. Purification for analysis failed due to the inseparable impurities: mp 130–132.5 °C; ^1H NMR (CDCl_3) δ 2.04 (d, $J = 5.7$ Hz, CH, 1H), 2.17 (d, $J = 5.7$ Hz, CH, 1H), 3.68 (s, CH, 1H), 3.84 (s, CH, 1H), 6.65 (t, $J = 3.0$ Hz, CH, 1H), 6.79 (d, $J = 3.0$ Hz, CH, 1H), 6.84 (t, $J = 3.0$ Hz, CH, 1H), 7.00–7.21 (m, ArH, 9H); ^{13}C NMR (CDCl_3) δ 51.2, 55.1, 73.0, 126.80, 126.82, 127.3, 127.7, 129.2, 131.1, 131.8, 133.7, 135.9, 138.9, 140.9, 142.8, 142.9, 155.8. MS m/z (M^+) 276.

1,4-Dihydro-1,4-epoxy-1,4-diphenyl-2-[2-(phenylthio)phenyl]naphthalene (5a). A mixture of **3a** (0.29 g, 0.5 mmol), sodium methoxide (0.54 g, 1.0 mmol), and methanol (3 mL) was heated for 12 h at 50 °C. Recrystallization from Et_2O –acetone gave **5a** (0.24 g, 99.5%): mp 158–159 °C; ^1H NMR (CDCl_3) δ 6.77 (d, $J = 7.5$ Hz, 1H, ArH), 7.00–7.50 (m, 21H, ArH), 7.72 (d, $J = 7.5$ Hz, 2H, ArH). ^{13}C NMR (CDCl_3) δ 92.7, 95.3, 120.0, 120.8, 124.8, 125.0, 126.0, 127.21, 127.25, 127.86, 127.91, 127.97, 128.1, 128.3, 128.4, 128.6, 128.7, 129.1, 130.9, 132.2, 134.7, 135.4, 135.6, 135.8, 144.1, 151.1, 152.7, 156.9. Anal. Calcd for $\text{C}_{34}\text{H}_{24}\text{OS}$: C, 84.96; H, 5.03. Found: C, 84.73; H, 5.10.

JO020406P