Intramolecular Cyclization to 1-Phenyl-1-benzothiophenium Salts by Electrophilic Addition of *o*-(Phenylsulfanyl)phenylalkynes

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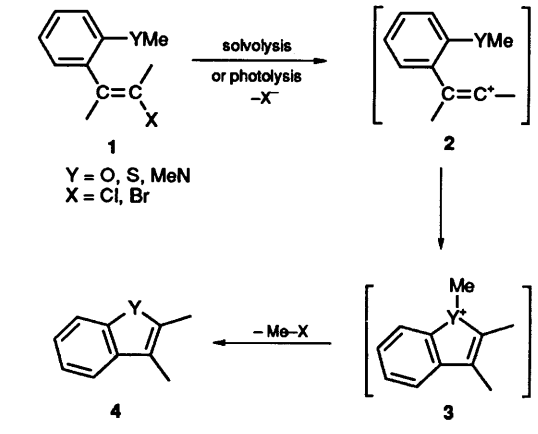
Electrophilic addition of 1-[*o*-(phenylsulfanyl)phenyl]-2-(*p*-methoxyphenyl)ethyne with electrophiles such as perchloric acid, tetrafluoroboric acid, bromine, and benzenesulfenyl chloride gave 1-phenyl-1-benzothiophenium salts exclusively. The substituent effect on the intramolecular cyclization with electrophiles has been examined. The aryl-substituted alkynes afforded predominantly the cyclized 1-phenyl-1-benzothiophenium salts but methyl-substituted alkynes yielded a mixture of the cyclized salt and the 1,2-addition product. In addition to the intramolecular cyclization at the intermediate vinyl cation or bridged ion, it is proposed, on the basis of the product from the reaction of methyl-substituted alkyne, that the π complex partly participates in the intramolecular cyclization.

Mechanistic and synthetic aspects of reactive intermediate vinyl cations have been investigated extensively.[1] Vinyl cations possessing heteroatoms are especially useful for the synthesis of heterocyclic compounds,[2] and the syntheses of benzofurans, benzothiophenes and indoles.[2f–i]

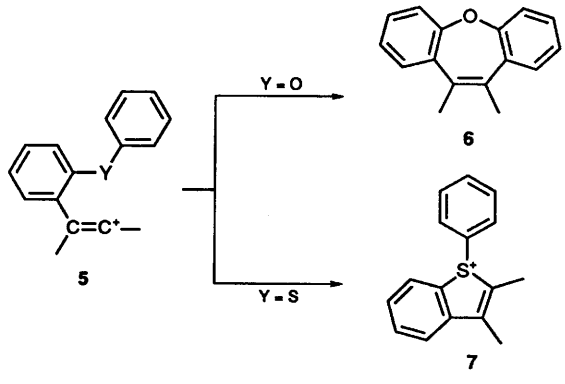
Electrophilic addition to carbon–carbon triple bonds, one of the ways for generating vinyl cations,[1] provides a simple method under mild conditions to conduct the present reaction. β-Arylvinyl cations substituted by methyl heteroatom at the *ortho* position undergo intramolecular cyclization followed by demethylation to give heterocyclic compounds as shown in Scheme 1. In our preliminary work,[2l] however, the phenyl heteroatom (oxygen and sulfur)-substituted arylvinyl cations showed two distinct intramolecular cyclizations at the aryl group and at the heteroatom, respectively (Scheme 2). This example shows that heteroatoms play a significant role in the cyclization of vinyl cations. In this paper, we describe further details of the intramolecular cyclization by electrophilic addition of *o*-(phenylsulfanyl)phenylalkynes. The competing formation of 1-phenyl-1-benzothiophenium ions is discussed with respect to the substituent and the kinds of the electrophile (Scheme 3).

Intramolecular Cyclization to 1-Phenyl-1-benzothiophenium Ions.—Although many cyclic sulfonium ions have been reported,[3] formation of unsaturated cyclic sulfonium ions related to the reaction of vinyl cations is limited to examples such as the thiirenium ions **11**,[2d,e,4] the thiethenium ions **12**[5] and the thiophenium ions **13**;† this suggests that the intramolecular reaction is a very convenient approach to prepare the ions **11**–**13**.

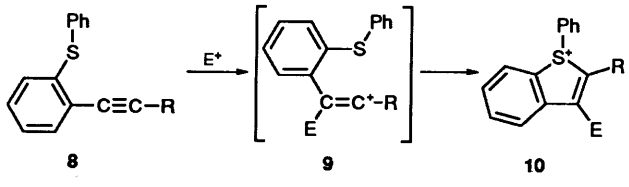
1-Benzothiophenium ions **3** (Y = S) similar to **13** are proposed[2f,h] as the intermediates in the reaction shown in Scheme 1 but are not isolable. However, since use of mild reaction conditions and introduction of an aryl group instead of a methyl group held out the possibility of allowing the 1-benzothiophenium ions to be isolated, electrophilic addition of 1-(4-methoxyphenyl)-2-[*o*-(phenylsulfanyl)phenyl]ethyne **14** was examined.



Scheme 1



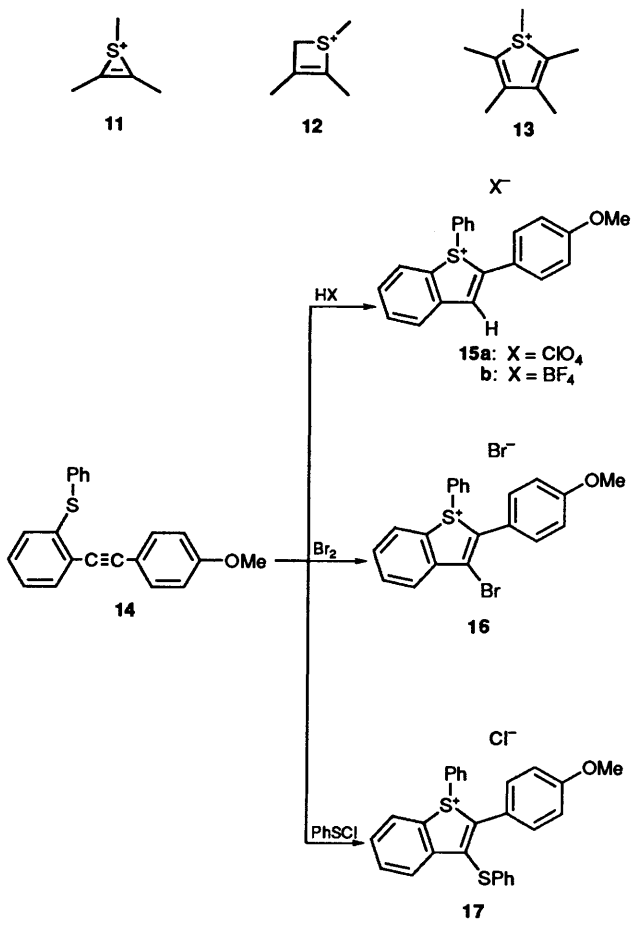
Scheme 2



Scheme 3

Treatment of the ethyne **14** with perchloric acid ($HClO_4$) and tetrafluoroboric acid (HBF_4) in dichloromethane–acetic acid gave 2-(4-methoxyphenyl)-1-phenyl-1-benzothiophenium per-

† Attempts to prepare *S*-alkylthiophenium ions **13** by participation of the sulfur atom were unsuccessful. Such *S*-alkylthiophenium and *S*-alkyl-1-benzothiophenium salts were prepared by alkylation of the corresponding thiophenes and 1-benzothiophenes, respectively.[6]



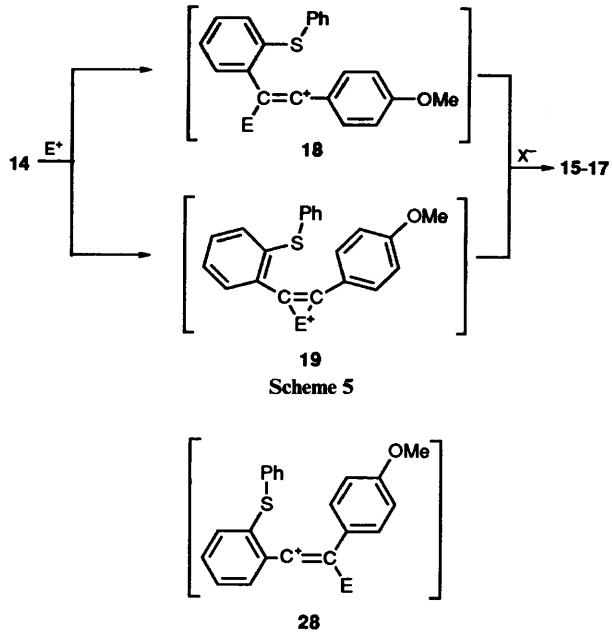
Scheme 4

chlorate **15a** and tetrafluoroborate **15b** in 73 and 63% yields, respectively (Scheme 4). No other products were detected.

Similar treatment of the alkyne **14** with bromine or benzenesulfenyl chloride in dichloromethane afforded 3-bromo-2-(*p*-methoxyphenyl)-1-phenyl-1-benzothiophenium bromide **16** or 2-(*p*-methoxyphenyl)-1-phenyl-3-(phenylsulfanyl)-1-benzothiophenium chloride **17**, respectively, in 85 or 81% yield (Scheme 4).

Electrophilic addition of an electrophile such as H^+, Br^+, or PhS^+ to the carbon–carbon triple bond produces a vinyl cation **18** or a bridged ion **19** (Scheme 5). Intramolecular cyclization usually competes with intermolecular attack of the counter anion. However, the present case provides 1-phenyl-1-benzothiophenium salts exclusively. Compared with the reaction of the corresponding *o*-(phenoxy)phenylalkynes,[2m] the high nucleophilicity and large van der Waals radius of sulfur are the reasons for causing the exclusive intramolecular attack of the sulfur, although the proximity of the sulfur to the reactive cationic centre and the less activation of the aromatic ring by sulfur also contribute the favourable formation of 1-phenyl-1-benzothiophenium ions.

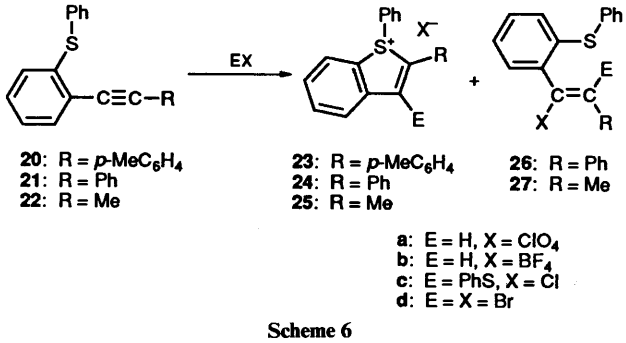
Effects of Substitutions and Electrophiles on the Cyclization.— In the reaction of the alkyne **14**, the intermediate vinyl cations **18** are greatly stabilized by the α *p*-methoxyphenyl group.[1] Accordingly, the contribution of the other possible vinyl cations, **28**, is negligible in the electrophilic addition. However, the less electron-donating groups such as tolyl, phenyl, and methyl groups should also affect the contribution of the intermediate ions such as **18**, **19** and **28**, since the phenylsulfanyl group is a good electron-donating group, although weaker than a methoxy group.[7]



Scheme 5

Reaction of several substituted *o*-(phenylsulfanyl)phenylalkynes **20**–**22** was investigated to determine the substituent effect with various electrophiles such as $HClO_4$, HBF_4, PhSCl, and Br_2 (Scheme 6). Reaction of the alkynes **20** and **21** with $HClO_4$ or HBF_4 at room temperature under conditions similar to those used for **14** resulted in recovery of the starting alkynes **20** and **21** or a very low yield of the products. This result is attributed to the relatively low reactivity of the alkynes **20** and **21** compared with the alkyne **14**.[8] The reaction of the alkynes **20** and **21** at reflux temperature for 12 h provided the 1-phenyl-1-benzothiophenium salts **23** and **24** in 53–89% yield.

Benzenesulfenyl chloride and bromine which are more reactive than $HClO_4$ or HBF_4 as evidenced by their reactions proceeding at room temperature, reacted with the aryl-substituted alkynes **20** and **21** to yield predominantly the cyclized 1-phenyl-1-benzothiophenium salts **23** and **24**; this is similar to the reactions with $HClO_4$ or HBF_4. The methyl-substituted alkyne **22** afforded in a similar reaction a mixture of the cyclized products **25** and addition products **27**. The results are summarized in Table 1.



Scheme 6

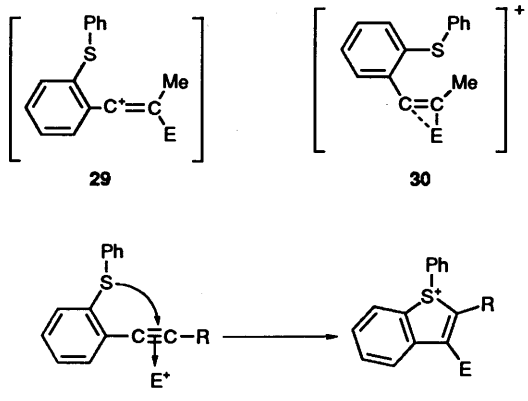
Compared with the corresponding oxygen analogue, *o*-(phenoxy)phenylalkynes, the cyclization process is easier than the addition process in the present case. However, it is noteworthy that the intramolecular cyclization takes place even with the methyl-substituted alkyne **22**. No such intramolecular cyclization was observed with the corresponding *o*-(phenoxy)-phenylalkynes which provide only alkene derivatives—addition products.

Formation of 1-phenyl-1-benzothiophenium salts with

Table 1 Effect of substituents and electrophiles on intramolecular cyclization of *o*-(phenylsulfanyl)phenylalkynes

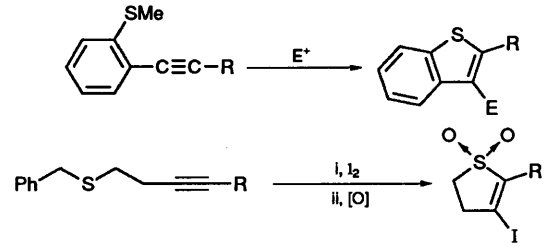
Substituent of alkyne R	Electrophile EX	Products (isolated yield, %) Cyclized product	Adduct
p-MeC_6H_4 **20**	$HClO_4$	88 **23a**	0
	HBF_4	86 **23b**	0
	PhSCl	88 **23c**	0
	Br_2	93 **23d**	0
Ph **21**	$HClO_4$	89 **24a**	0
	HBF_4	53 **24b**	0
	PhSCl	58 **24c**	0
	Br_2	80 **24d**	10 **26d**
Me **22**	PhSCl	16 **25c**	60 **27c**
	Br_2	45 **25d**	19 **27d**

methyl-substituted alkynes cannot be explained by the mechanism shown in Scheme 5 since addition of electrophiles occurs at the carbon β to the (phenylsulfanyl)phenyl group to generate a vinyl cation **29** or an unsymmetrical bridged ion **30**. Species **29** and **30** cannot undergo intramolecular cyclization to produce the 1-phenyl-1-benzothiophenium ion, but afford the addition products **27** by intramolecular attack of X^-. The present result is best explained in terms of the intramolecular cyclization occurring early on at the stage when the ion **29** or **30** is formed: namely, at the π complex of the electrophile and the alkyne as shown in Scheme 7.*



Scheme 7

Taking into account its proximity, large van der Waals radius and high nucleophilicity, the sulfur atom can interact with the carbon–carbon triple bond complexed with an electrophile to yield the 1-phenyl-1-benzothiophenium ion directly. It is considered that this mechanism plays a significant role in the alkyl-substituted alkynes. Previously reported iodocyclization of alkene thioethers has been explained by interaction of the sulfur atom with the π complex on the basis of the kinetics and the products.[9] Similar cyclization in acetylenic systems have been observed in (*o*-methylsulfanylphenyl)alkynes[10,†] and acetylenic sulfides (Scheme 8).[11]



Scheme 8

In summary, we have disclosed a convenient preparation of 1-phenyl-1-benzothiophenium salts by electrophilic addition of electrophiles to *ortho*-(phenylsulfanyl) phenylalkynes. This procedure represents a simple synthesis under moderate conditions of 1-aryl-1-benzothiophenium salts. The advantage of this method over those previously reported is that the functional group can be introduced into the 3 position of 1-phenyl-1-benzothiophenium salts by the choice of suitable electrophiles.

Experimental

General methods were described previously.[2m] Copper(I) acetylides were prepared according to the method described by Castro *et al.*[12] Benzenesulfenyl chloride was prepared by the reaction of diphenyl disulfide with SO_2Cl_2.[13]

2-Iodophenyl Phenyl Sulfide.—To a solution of diphenyl sulfide (33.3 cm^3, 0.20 mol) in THF (100 cm^3) was added dropwise BuLi (1.6 mol dm^{-3} in hexane; 125 cm^3, 0.20 mol) at 0 °C under a nitrogen atmosphere. After being stirred for 4 h, the mixture was cooled to −70 °C and a solution of iodine (60 g, 0.24 mol) in THF (100 cm^3) was added to it. The mixture was warmed to room temperature with stirring and then quenched with aqueous sodium thiosulfate. The product was extracted with diethyl ether and the organic layer was washed, dried (Na_2SO_4) and evaporated to give an oil, which was submitted to column chromatography on alumina. Elution with hexane–dichloromethane gave an oil which crystallized. Recrystallization from methanol yielded the title compound, (14.24 g, 23%), m.p. 56–57 °C (lit.,[14] m.p. 55–56 °C); δ_H(60 MHz; $CDCl_3$) 6.68–7.92 (m, ArH).

Preparation of o-(*Phenylsulfanyl*)*phenylalkynes: General Procedure.*—A mixture of *o*-iodophenyl phenyl sulfide (3.21 g, 10 mmol) and a copper(I) acetylide (12 mmol) was refluxed in pyridine (40 cm^3) for 12 h. Dilute HCl and aqueous NH_4Cl were added to the cooled mixture which was then extracted with diethyl ether. The extract was washed successively with aqueous sodium thiosulfate, dilute HCl, water and saturated brine and then dried (Na_2SO_4) and evaporated. The product was purified by column chromatography on alumina with hexane–dichloromethane as the eluent.

1-(p-*Methoxyphenyl*)-2-[o-(*phenylsulfanyl*)*phenyl*]*ethyne* **14** (91%), m.p. 82–85 °C (from MeOH–EtOH) (Found: C, 79.5; H, 5.1. $C_{21}H_{16}OS$ requires C, 79.7; H, 5.1%); ν_{max}(Nujol)/cm^{-1} 2212 (C≡C); δ_H(250 MHz; $CDCl_3$) 3.80 (s, OMe) and 6.77–7.51 (m, ArH); δ_C(63 MHz; $CDCl_3$) 55.28, 85.99, 95.76, 113.96, 115.25, 123.44, 125.96, 127.85, 128.40, 129.39, 132.36, 132.92, 133.13, 133.79, 139.68 and 159.80; *m/z* 316 (M^+, 100%) and 301 (M^+ − Me, 29).

1-(p-*Methylphenyl*)-2-[o-(*phenylsulfanyl*)*phenyl*]*ethyne* **20** (66%), oil (Found: C, 83.9; H, 5.4. $C_{21}H_{16}S$ requires C, 84.0; H,

* A referee suggested the reversible formation of thiirenium ions analogous to **19** giving **25** and **27**. However, we cannot discard the participation of the π complex in the intramolecularcyclization of **22** for the following reasons. (1) 1-Alkyl-2-arylethynes, in the reaction with Br^+ or H^+, tend to produce the open ion **29** rather than bridged ions.[1,8] (2) Additional experiments of 1-[*o*-(phenylsulfanyl)phenyl]hex-1-yne with $HClO_4$ and HBF_4 gave 2-butyl-1-phenyl-1-benzothiophenium perchlorate and tetrafluoroborate, respectively, in 47 and 43% yields.

† Treatment of 1-aryl-2-[2-(methylsulfanyl)phenyl]ethynes **31** with electrophiles gave 1-benzothiophenes **32** quantitatively.

5.4%); ν_{max}(neat)/cm^{-1} 2212 (C≡C); δ_H(250 MHz; $CDCl_3$) 2.29 (s, Me) and 6.97–7.51 (m, ArH); δ_C(63 MHz; $CDCl_3$) 21.47, 86.55, 95.88, 119.95, 123.05, 125.82, 127.85, 128.50, 128.60, 129.00, 129.35, 131.47, 132.38, 132.97, 133.53, 138.48 and 139.90.

1-*Phenyl*-2-[o-(*phenylsulfanyl*)*phenyl*]*ethyne* **21** (59%), oil (Found: C, 83.8; H, 4.9. $C_{20}H_{14}S$ requires C, 83.9; H, 4.9%); ν_{max}(neat)/cm^{-1} 2216 (C≡C); δ_H(250 MHz; $CDCl_3$) 6.98–7.53 (m, ArH); δ_C(63 MHz; $CDCl_3$) 87.16, 95.61, 122.86, 123.02, 125.87, 127.91, 128.24, 128.39, 128.67, 128.71, 129.39, 131.59, 132.50, 133.00, 133.47 and 140.05; *m/z* 286 (M^+, 100%).

1-[o-(*Phenylsulfanyl*)*phenyl*]*prop*-1-*yne* **22**.—NaOMe (108 mg, 2.0 mmol) was added to a solution of 2-methyl-1-phenyl-1-benzothiophenium triflate[15] (2.0 mmol) in MeOH (20 cm^3) at room temperature and the mixture was stirred for 12 h at room temperature. Evaporation of the mixture provided a residue which was submitted to column chromatography on alumina. Elution with dichloromethane gave the *title compound* **22** (99%), m.p. 38–39 °C (Found: C, 80.1; H, 5.3. $C_{15}H_{12}S$ requires C, 80.3; H, 5.4%); ν_{max}(neat)/cm^{-1} 2232 (C≡C); δ_H(250 MHz; $CDCl_3$) 2.05 (s, Me) and 6.89–7.46 (m, ArH); δ_C(63 MHz; $CDCl_3$) 4.56, 77.59, 92.54, 123.35, 125.64, 127.93, 128.01, 128.16, 129.34, 132.53, 133.25, 133.45 and 139.77.

Reaction of 1-(p-*Methoxyphenyl*)-2-[o-(*phenylsulfanyl*)*phenyl*]*ethyne* **14** *with Electrophiles*.—The alkyne **14** (0.316 g, 1.0 mmol) was dissolved in CH_2Cl_2 (2 cm^3) and acetic acid (8 cm^3) was added to the solution. The solution was then stirred whilst $HClO_4$ (60%; 0.15 cm^3, 1.5 mmol) or HBF_4 (42%; 0.24 cm^3, 1.5 mmol) was added dropwise to it at room temperature. After the mixture had been stirred at room temperature for 12 h it was extracted with CH_2Cl_2, and the extract was washed successively with water and saturated brine and then dried (Na_2SO_4) and evaporated. The residue crystallized upon addition of diethyl ether to it. The crystals were filtered off and dried *in vacuo*.

In the reactions with PhSCl and with Br_2, a solution of each (1.0 mmol) in CH_2Cl_2 (2 cm^3) was added dropwise at room temperature to a stirred solution of **14** (1.0 mmol) in CH_2Cl_2 (10 cm^3) and the reaction mixture was stirred for 12 h. After evaporation of each reaction mixture the resulting residue was submitted to column chromatography on alumina. Elution with CH_2Cl_2–EtOH gave the product which crystallized upon addition of diethyl ether to it. The crystals were filtered off and dried *in vacuo*. Some of the benzothiophenium salts **23c**, **23d** and **25c** provided unsatisfactory combustion analyses because of their highly hygroscopic nature.

2-[p-(*Methoxyphenyl*)]-1-*phenyl*-1-*benzothiophenium perchlorate* **15a** (73%), m.p. 189–191 °C (from CH_2Cl_2–diethyl ether) (Found: C, 60.1; H, 4.2. $C_{21}H_{17}ClO_5S$ requires C, 60.5; H, 4.1%); δ_H(400 MHz, $CDCl_3$–[$^2H_6$]DMSO) 3.81 (s, 3 H, OMe) and 6.91–8.21 (m, 14 H, ArH); δ_C(100 MHz, $CDCl_3$–[$^2H_6$]DMSO) 55.39, 115.18, 119.63, 123.89, 127.09, 127.62, 129.07, 130.01, 130.31, 131.24, 131.54, 133.42, 134.11, 134.97, 141.97, 142.73 and 161.58.

2-[p-(*Methoxyphenyl*)]-1-*phenyl*-1-*benzothiophenium Tetrafluoroborate* **15b** (63%), m.p. 187–189 °C (from CH_2Cl_2–diethyl ether) (Found: C, 62.1; H, 4.2. $C_{21}H_{17}BF_4OS$ requires C, 62.4; H, 4.2%); δ_H(400 MHz, $CDCl_3$–[$^2H_6$]DMSO) 3.80 (s, 3 H, OMe) and 6.91–8.21 (m, 14 H, ArH); δ_C(100 MHz, $CDCl_3$–[$^2H_6$]DMSO) 55.37, 115.18, 119.63, 123.86, 127.09, 127.61, 129.05, 130.01, 130.30, 131.25, 131.54, 133.41, 134.11, 134.91, 141.97, 142.71 and 161.58.

3-*Bromo*-2-[p-(*methoxyphenyl*)]-1-*phenyl*-1-*benzothiophenium bromide* **16** (85%), m.p. 115–120 °C (decomp., hygroscopic, from CH_2Cl_2–diethyl ether) (Found: C, 52.6; H, 3.3. $C_{21}H_{16}Br_2OS$ requires C, 53.0 H, 3.4%); δ_H(250 MHz, $CDCl_3$) 3.82 (s, 3 H, OMe), 6.95–8.00 (m, 12 H, ArH) and 9.05 (d, *J* 7, 1 H, ArH); δ_C(63 MHz, $CDCl_3$) 55.61, 115.15, 118.24, 122.36, 124.34, 126.48, 130.26, 131.00, 131.26, 131.34, 131.54, 134.55, 134.77, 136.89, 141.62 and 161.88.

2-[p-(*Methoxyphenyl*)]-1-*phenyl*-3-(*phenylsulfanyl*)-1-*benzothiophenium chloride* **17** (81%), m.p. 107–111 °C (decomp., hygroscopic, from CH_2Cl_2–diethyl ether) (Found: C, 69.9; H, 4.5. $C_{27}H_{21}ClOS_2$ requires C, 70.3; H, 4.6%); δ_H(250 MHz, $CDCl_3$) 3.78 (s, 3 H, OMe), 6.95–7.84 (m, 17 H, ArH) and 9.01 (d, *J* 5, 1 H, ArH); δ_C(63 MHz, $CDCl_3$) 55.52, 114.75, 119.04, 125.65, 126.17, 128.25, 129.66, 130.18, 130.26, 130.50, 130.79, 130.90, 131.18, 132.01, 132.34, 133.64, 134.34, 136.49, 141.24, 142.59 and 161.73.

2-(p-*Methylphenyl*)-1-*phenyl*-1-*benzothiophenium perchlorate* **23a** (88%), m.p. 211–213 °C (Found: C, 62.7; H, 4.3. $C_{21}H_{17}ClO_4S$ requires C, 62.7; H, 4.3); δ_H(250 MHz, $CDCl_3$–[$^2H_6$]DMSO) 2.40 (s, 3 H, Me) and 7.22–8.28 (m, 14 H, ArH); δ_C(63 MHz, $CDCl_3$–[$^2H_6$]DMSO) 21.31, 123.01, 124.17, 127.25, 127.60, 130.38, 130.52, 131.80, 132.70, 133.07, 134.35, 135.28, 141.73, 141.97 and 142.20.

2-(p-*Methylphenyl*)-1-*phenyl*-1-*benzothiophenium tetrafluoroborate* **23b** (86%), m.p. 186–188 °C (Found: C, 64.9; H, 4.6. $C_{21}H_{17}BF_4S$ requires C, 65.0; H, 4.4); δ_H(250 MHz, $CDCl_3$–[$^2H_6$]DMSO) 2.27 (s, 3 H, Me) and 7.19–8.31 (m, 14 H, ArH); δ_C(63 MHz, $CDCl_3$–[$^2H_6$]DMSO) 20.97, 123.70, 124.43, 127.11, 127.22, 127.55, 130.13, 130.29, 131.35, 131.40, 132.59, 133.90, 134.70, 134.79, 141.16, 142.04 and 142.39.

2-(p-*Methylphenyl*)-1-*phenyl*-3-(*phenylsulfanyl*)-1-*benzothiophenium chloride* **23c** (93%), m.p. 123–126 °C (decomp., hygroscopic); δ_H(250 MHz, $CDCl_3$) 2.29 (s, 3 H, Me), 7.13–7.64 (m, 17 H, ArH) and 9.02 (d, *J* 6, 1 H, ArH); δ_C(63 MHz, $CDCl_3$) 21.41, 123.89, 125.18, 126.31, 128.26, 129.58, 129.82, 130.07, 130.33, 130.49, 130.55, 130.78, 130.93, 131.17, 132.45, 133.67, 134.43, 138.10, 140.57, 141.71 and 142.24.

3-*Bromo*-2-(p-*methylphenyl*)-1-*phenyl*-1-*benzothiophenium bromide* **23d** (88%), m.p. 120–123 °C (decomp., hygroscopic); δ_H(250 MHz, $CDCl_3$) 2.35 (s, 3 H, Me), 7.19–8.13 (m, 12 H, ArH) and 9.15 (d, *J* 6, 1 H, ArH); δ_C(63 MHz, $CDCl_3$) 21.56, 123.39, 123.46, 124.27, 126.57, 129.68, 130.34, 130.61, 131.05, 131.25, 131.30, 131.46, 134.53, 134.73, 137.06, 141.48 and 142.28.

1,2-*Diphenyl*-1-*benzothiophenium perchlorate* **24a** (88%), m.p. 210–212 °C (Found: C, 61.8; H, 4.0. $C_{20}H_{15}ClO_4S$ requires C, 62.1; H, 3.9); δ_H(250 MHz, $CDCl_3$–[$^2H_6$]DMSO) 7.47–8.56 (m, 15 H, ArH); δ_C(63 MHz, $CDCl_3$–[$^2H_6$]DMSO) 124.40, 127.36, 127.41, 127.60, 127.75, 129.67, 130.52, 130.80, 131.46, 133.76, 134.05, 134.62, 134.74, 142.53 and 142.68.

1,2-*Diphenyl*-1-*benzothiophenium tetrafluoroborate* **24b** (53%), m.p. 183–187 °C (Found: C, 64.0; H, 4.1. $C_{20}H_{15}BF_4S$ requires C, 64.2; H, 4.0); δ_H(250 MHz, [$^2H_6$]DMSO) 7.86–8.95 (m, 15 H, ArH); δ_C(63 MHz, $CDCl_3$–[$^2H_6$]-DMSO) 124.42, 127.36, 127.42, 127.62, 127.75, 129.68, 130.52, 130.81, 131.47, 133.76, 134.06, 134.64, 134.75, 142.55 and 142.69.

1,2-*Diphenyl*-3-(*phenylsulfanyl*)-1-*benzothiophenium chloride* **24c** (58%), m.p. 105–110 °C (decomp., hygroscopic) (Found: C, 72.0; H, 4.35. $C_{26}H_{19}ClS_2$ requires C, 72.4; H, 4.4); δ_H(60 MHz, $CDCl_3$) 7.07–7.94 (m, 18 H, ArH) and 8.99 (d, *J* 5, 1 H, ArH).

3-*Bromo*-1,2-*diphenyl*-1-*benzothiophenium bromide* **24d** (80%), m.p. 122–128 °C (decomp., hygroscopic) (Found: C, 53.4; H, 3.4. $C_{20}H_{14}Br_2S$ requires C, 53.8; H, 3.2); δ_H(60 MHz, $CDCl_3$) 7.24–8.09 (m, 13 H, ArH) and 8.92 (d, *J* 7, 1 H, ArH).

2-*Methyl*-1-*phenyl*-3-(*phenylsulfanyl*)-1-*benzothiophenium chloride* **25c** (16%), hygroscopic crystals; δ_H(250 MHz, $CDCl_3$), 2.43 (s, 3 H, Me), 7.03–7.89 (m, 13 H, ArH) and 8.68 (d, *J* 8, 1 H, ArH); δ_C(63 MHz, $CDCl_3$) 20.77, 124.08, 125.74, 128.45, 129.38, 129.87, 130.35, 130.51, 131.05, 131.53, 131.97, 132.12, 133.69, 134.80, 139.69, 140.46 and 141.65.

3-*Bromo*-2-*methyl*-1-*phenyl*-1-*benzothiophenium bromide* **25d**

(45%), m.p. 213–317 °C (decomp.) (Found: C, 46.7, H. 3.1. $C_{15}H_{12}Br_2S$ requires C, 46.9; H, 3.15); δ_H(250 MHz, $CDCl_3$) 2.47 (s, 3 H, Me), 7.61–8.00 (m, 8 H, ArH) and 8.78 (d, *J* 8, 1 H, ArH); δ_C(63 MHz, $CDCl_3$) 14.12, 122.79, 126.02, 127.57, 129.34, 131.15, 131.29, 131.36, 131.64, 133.90, 134.46, 135.18 and 140.29.

1,2-*Dibromo*-1-*phenyl*-2-[o-(*phenylsulfanyl*)*phenyl*]*ethene* **26d** (10%), oil (Found: C, 53.6; H, 3.1. $C_{20}H_{14}Br_2S$ requires C, 53.8; H, 3.2); δ_H(60 MHz, $CDCl_3$) 7.11–7.64 (m, ArH); *m*/*z* 448 (M^+ + 4, 2), 446 (M^+ + 2, 4), 444 (M^+, 2), 367 (M^+ − 79, 10), 365 (M^+ − 81, 10) and 286 (M^+ − 2Br, 100).

1-*Chloro*-2-*phenylsulfanyl*-1-[o-(*phenylsulfanyl*)*phenyl*]*prop*-1-*ene* **27c** (60%), oil (Found: C, 68.4; H, 4.6. $C_{21}H_{17}ClS_2$ requires C, 68.4; H, 4.6); δ_H(250 MHz, $CDCl_3$) 2.16 (s, 3 H, Me) and 7.03–7.44 (m, 14 H, ArH); δ_C(63 MHz, $CDCl_3$) 20.77, 126.61, 127.04, 127.37, 127.57, 128.90, 129.22, 129.39, 129.98, 130.75, 131.04, 131.21, 132.56, 133.90, 134.66, 136.45 and 139.21; *m*/*z* 368 (M^+, 6), 259 (M^+ − PhS, 100) and 224 (M^+ − PhSCl, 94).

1,2-*Dibromo*-1-[o-(*phenylsulfanyl*)*phenyl*]*prop*-1-*ene* **27d** (19%) (a 82:18 mixture of *E* and *Z* isomers), oil (Found: C, 47.2; H, 3.4. $C_{15}H_{12}Br_2S$ requires C, 46.9; H, 3.15); δ_H(250 MHz, $CDCl_3$) (*E* and *Z* isomers) 2.09 (s, Me), 2.59 (s, Me) and 7.09–7.47 (m, ArH).

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