Tetrahedron Vol. 49, No. 23, pp. 5055-5066, 1993
Printed in Great Britain

0040-4020/93 $6.00+.00

Intramolecular Cyclization of [*o*-(Arylthio)phenyl]ethenes. Synthesis and Crystal Structure of 1-Arylbenzo[b]thiophenium Salts

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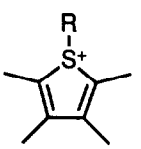
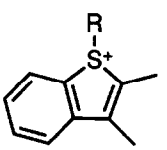
(*Received in Japan* 22 *March* 1993)

Abstract: Novel 1-arylbenzo[b]thiophenium salts (**4**) are prepared by bromine-induced intramolecular cyclization of [*o*-(arylthio)phenyl]ethenes (**3**). The substituent and solvent effects on the formation of the 1-arylbenzo[b]thiophenium salts **4** are described. The reaction with iodine monochloride provides the improved yields of 2-unsubstituted and 2-methyl-1-phenylbenzo[b]thiophenium salts **4**. The single crystal structure of 1,2,3-triphenylbenzo[b]thiophenium perchlorate (**4b**: X = ClO_4) shows that the bonds around the sulfur atom are arranged pyramidally. The sulfur-carbon bond length related to the non-fused phenyl ring is 1.784 Å and the S-C bond lengths in the five-membered ring are 1.762 and 1.790 Å. The bond angles around sulfur are 92.1, 103.1, and 107.0°. The relatively short interatomic distance (3.092 Å) between the sulfur and the oxygen of the perchlorate anion is observed.

Although thiophenium (**1**) and benzo[b]thiophenium (**2**) salts have been prepared, most of the preparations involve the alkylation of thiophenes and benzo[b]thiophenes with alkyl halides in the presence of silver salts.[1] Accordingly, these salts **1** and **2** are generally dealkylated on treatment even with weak nucleophiles.[1] It is expected that introduction of an aryl group instead of an alkyl group on the sulfur atom will stabilize salts **1** and **2** since the aryl carbon-sulfur bond is much stronger than the alkyl carbon-sulfur bond.[2] However, the general preparation of such S-arylated salts (**1** and **2**: R = aryl) has not been reported so far.[3]



(**1**)



(**2**)

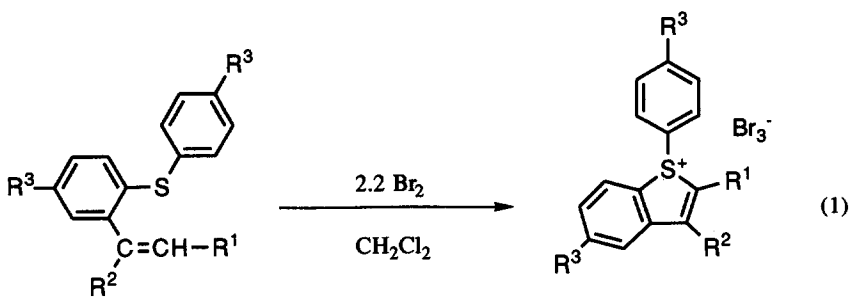
Neighboring group participation in electrophilic addition of alkenes has been well studied.[4] Especially, the participation by sulfide groups is synthetically interesting because the cyclization produces a cyclic sulfonium ion.[5] In our continuing study on solvolysis and photolysis of arylvinyl halides to lead to intramolecular cyclization,[6] we found that bromination of [*o*-(arylthio)phenyl]ethenes (**3**) caused participation of the sulfur atom to form a 1-arylbenzo[b]thiophenium bromide (**4**).[7] This procedure provides a convenient method for preparing 1-arylbenzo[b]thiophenium salts. Thus, we describe here the preparation of 1-arylbenzo[b]thiophenium salts and

also a single crystal structure of the 1-arylbenzo[b]thiophenium salt in detail.

RESULTS AND DISCUSSION

Formation of 1-Arylbenzo[b]thiophenium Tribromides (4: X = Br_3).

Generally alkenes react with an equimolar amount of bromine to yield 1,2-adducts.[8] However, treatment of 1,2-diphenyl-1-[2-(phenylthio)phenyl]ethene (**3b**) with an equimolar amount of bromine gave an incomplete bromination of the alkene. Treatment of **3b** with 2.2 molar amounts of bromine gave orange crystals of 1,2,3-triphenylbenzo[b]thiophenium tribromide (**4b**: X = Br_3). The benzo[b]thiophenium tribromide **4b** (X = Br_3) easily released a bromine molecule. Thus, addition of **4b** (X = Br_3) to a solution of 1,1-diphenylethene in $CDCl_3$ yielded 1,2-dibromo-1,1-diphenylethane[9] and 1,2,3-triphenylbenzo[b]thiophenium bromide (**4b**: X = Br). Also, passing **4b** (X = Br_3) through a column of alumina with ethanol as the solvent or refluxing **4b** (X = Br_3) in ethanol afforded **4b** (X = Br). Similarly, bromination of [*o*-(arylthio)phenyl]ethenes **3a**, **3b**, and **3f** with 2.2 equimolar amounts of bromine yielded the corresponding 1-arylbenzo[b]thiophenium tribromides **4a** (X = Br_3), **4b** (X = Br_3), and **4f** (X = Br_3), respectively.



(1)

3

a: $R^1 = R^2$ = Ph, R^3 = Me
b: $R^1 = R^2$ = Ph, R^3 = H
f: R^1 = Me, R^2 = Ph, R^3 = H

4 (X = Br_3)

a: $R^1 = R^2$ = Ph, R^3 = Me (100%)
b: $R^1 = R^2$ = Ph, R^3 = H (100%)
f: R^1 = Me, R^2 = Ph, R^3 = H (30%)

Preparation of 1-Arylbenzo[b]thiophenium Salts (4).

Use of excess bromine gives rise to a complete bromine-induced cyclization. The benzo[b]thiophenium tribromides **4** (X = Br_3) can be readily transformed to the corresponding stable monobromides **4** (X = Br). However, the substituent on the double bond should also affect the bromine-induced cyclization, as has been discussed in the electrophilic addition to alkenes.[10] Then, we examined the substituent effect on the bromination of [*o*-(arylthio)phenyl]ethenes **3** together with the solvent effect with emphasis being placed on the scope and limitation of preparation of the 1-arylbenzo[b]thiophenium salts **4**.

Brominations of **3** were conducted in CCl_4, CH_2Cl_2, and AcOH with 1.1 or 2.2 equimolar amounts of bromine. The product distributions were determined after purification by column chromatography on alumina. Most of brominations of various substituted [*o*-(arylthio)phenyl]ethenes **3** resulted the formation of expected 1-arylbenzo[b]thiophenium bromides **4** (X = Br) as the major product but the reaction also provided bromoethenes (**5**) which were derived by addition of bromine and the subsequent elimination of hydrogen bromide. The

formation of **4** (**X = Br**) depends upon the solvent polarity and the substituent as shown in Table 1.

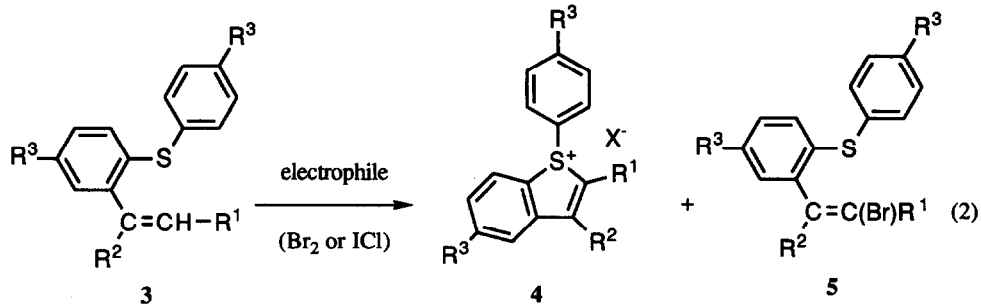


Table 1. 1-Arylbenzo[b]thiophenium Salts (**4**) from [*o*-(Arylthio)phenyl]ethenes (**3**).

entry		**3** R^1	R^2	R^3	electrophile (equiv)	solvent	yields (%) of products after workup[a] **4**		others
1	**a**	Ph	Ph	Me	Br_2 (1.1)	CCl_4	26	**a** (X=Br)	60 (**3a**)
2					(1.1)	CH_2Cl_2	51	**a** (X=Br)	42 (**3a**)
3					(2.2)	CH_2Cl_2	100	**a** (X=Br)	-
4					(1.1)	AcOH	57	**a** (X=Br)	39 (**3a**)
5	**b**	Ph	Ph	H	Br_2 (2.2)	CH_2Cl_2	100	**b** (X=Br)	-
6	**c**	Ph	An[b]	H	Br_2 (1.1)	CCl_4	36	**c** (X=Br)	10 (**3c**); 47 (**5c**)
7					(1.1)	CH_2Cl_2	50	**c** (X=Br)	9 (**3c**); 32 (**5c**)
8	**d**	An[b]	Ph	H	Br_2 (1.1)	CCl_4	84	**d** (X=Br)	16 (**3d**)
9					(1.1)	CH_2Cl_2	85	**d** (X=Br)	14 (**3d**)
10	**e**	Ph	Me	H	Br_2 (1.1)	CCl_4	94	**e** (X=Br)	-
11					(1.1)	CH_2Cl_2	100	**e** (X=Br)	-
12	**f**	Me	Ph	H	Br_2 (1.1)	CCl_4	22	**f** (X=Br)	25 (**3f**); 43 (**5f**)
13					(1.1)	CH_2Cl_2	49	**f** (X=Br)	47 (**5f**)
14					(1.1)	AcOH	39	**f** (X=Br)	53 (**5f**)
15					ICl (1.1)	CH_2Cl_2	85[c]	**f** ($X=ClO_4$)	-[d]
16	**g**	H	Ph	H	Br_2 (1.1)	CCl_4	0	**g** (X=Br)	94 (**5g**)
17					(1.1)	CH_2Cl_2	31	**g** (X=Br)	60 (**5g**)
18					(1.1)	AcOH	47	**g** (X=Br)	47 (**5g**)
19					ICl (1.1)	CH_2Cl_2	71[c]	**g** ($X=ClO_4$)	-[d]

(a) Isolated yields by column chromatography on alumina. (b) *p*-$MeOC_6H_4$. (c) Isolated as the perchlorate by treatment with silver perchlorate. (d) Not determined.

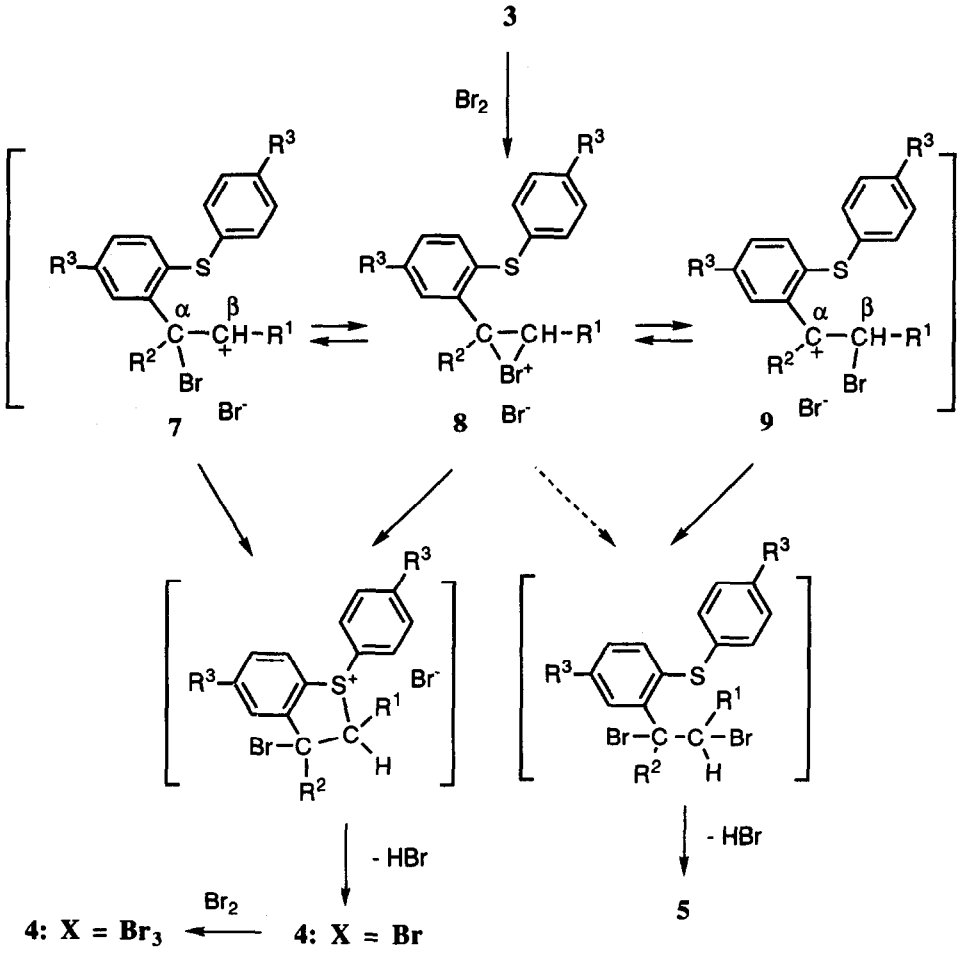
Unreacted [*o*-(arylthio)phenyl]ethenes **3** were recovered in the cases of congested triarylethenes **3a**, **3c**, and **3d**. This suggests that the formation of 1-arylbenzo[b]thiophenium tribromides **4** (**X = Br_3**) consumes bromine partially and prevents the bromination.

Table 1 shows the following orders for the ease of the formation of 1-arylbenzo[b]thiophenium bromides **4** (**X = Br**): substituent R^1; An ~ Ph > Me > H, substituent R^2; Me > Ph > An, and solvent; AcOH > CH_2Cl_2 > CCl_4.

The reaction process is determined by competition of the intramolecular cyclization by sulfur with the intermolecular substitution by bromide ion as shown in Scheme 1. Accordingly, the reaction is governed by the following factors; (1) the charge population on the α or β carbon in the intermediate bromonium ion and (2) the polarity of the solvent, as has been discussed in the brominations.[10,11]

Substituents (R^1 and R^2) strongly affect the relative population of the intermediate ions **7**, **8**, and **9**.[10,11] Phenyl and *p*-methoxyphenyl (An) groups on the β carbon stabilize the ion **7** and yield the cyclized product **4** (**X** = **Br**) predominantly, while, in the case of methyl group and hydrogen atom, a large contribution of the ion **9** becomes predominant to give the vinyl bromide **5** selectively. The formation of the cyclized product **4** in small amounts in these cases should be derived from the bridged intermediate **8**. Similarly, An on the α carbon, stabilizing the ion **9**, produces the vinyl bromide **5** but An on the β carbon yields the cyclized product **4** (**X** = **Br**) via the ion **7**. 1-Phenyl-2-[2-(phenylthio)phenyl]prop-1-ene (**3e**), where ion **7** is a large contributor, leads to **4e** (**X** = **Br**) predominantly. The participation by sulfur in the early stage of a bromine-π complex may be also possible.[5b]

Scheme 1. Possible reaction path in bromination of **3**



Solvent effect on the product distribution may be attributed to the polarity of the solvent employed. Polar solvents favor the formation of a loose ion pair, i.e., a loose bromonium cation and bromide anion pair, compared with non-polar solvents in which a tight ion pair is formed.[12] The intramolecular attack of the sulfur atom precedes the intermolecular attack of bromide anion in the loose ion pair, whereas the attack of bromide anion is favorable in the tight ion pair because of the proximity of bromide anion.

Bromine-induced cyclization was not selective in the cases of [*o*-(arylthio)phenyl]ethenes **3f** and **3g** and provided both products from intramolecular attack of sulfur atom and from intermolecular attack of bromide anion. To accomplish the high selective intramolecular cyclization by sulfur atom, a good electrophile, iodine monochloride (ICl) was used.[13] Treatment of [*o*-(phenylthio)phenyl]ethenes **3f** and **3g** with ICl followed by reaction with silver perchlorate gave 1-phenylbenzo[b]thiophenium perchlorates **4f** (X = ClO_4) and **4g** (X = ClO_4) in 85 and 71% yields, respectively (entries 15 and 19). These results are explained by the unique property that iodine monochloride forms a pair of a stable iodonium ion and a less nucleophilic chloride anion pair in comparison with those of bromine.

Crystal Structure of a 1-Arylbenzo[b]thiophenium Salt 4.

To establish the exact molecular structure of a 1-arylbenzo[b]thiophenium salt, an X-ray structural analysis was conducted. Most of 1-arylbenzo[b]thiophenium bromides did not give a suitable crystal for the X-ray analysis since they were hygroscopic and amorphous solids in most cases. Then, 1,2,3-triphenylbenzo[b]thiophenium bromide (**4b**: X = Br) was converted to the perchlorate (**4b**: X = ClO_4) by use of silver perchlorate. A single crystal of 1,2,3-triphenylbenzo[b]thiophenium perchlorate (**4b**: X = ClO_4) was grown by a slow evaporation of a mixed solvent of CH_2Cl_2 and CCl_4. The structural data are given in Table 2 and the ORTEP drawing is depicted in Figure 1.

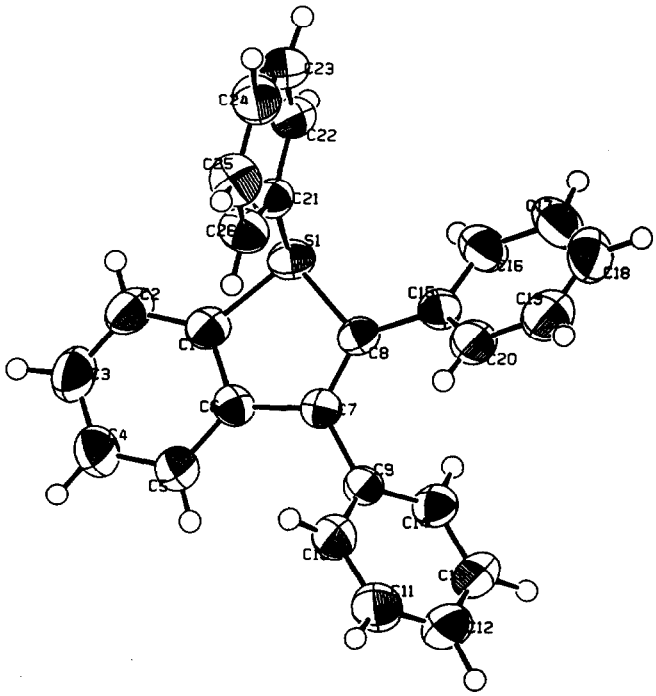


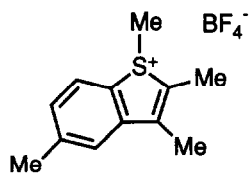
Figure 1. ORTEP representation of **4b** (X = ClO_4) (50.0% probability ellipsoids).

Table 2. Selected Interatomic Distances and Bond Angles[a]

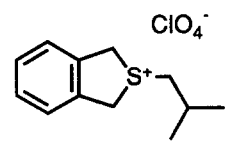
	Interatomic Distances (Å)		
S(1) – C(1)	1.762(4)	C(4) – C(5)	1.393(5)
S(1) – C(8)	1.790(3)	C(5) – C(6)	1.382(4)
S(1) – C(21)	1.784(3)	C(6) – C(7)	1.471(4)
C(1) – C(2)	1.377(5)	C(7) – C(8)	1.346(4)
C(1) – C(6)	1.400(4)	S(1) ...O(2)	3.092(3)
C(2) – C(3)	1.378(5)	O(2) ... C(8)	3.225(4)
C(3) – C(4)	1.369(6)		
	Bond Angles (deg)		
C(1) – S(1) – C(8)	92.1(1)	C(1) – C(6) – C(7)	113.2(3)
C(1) – S(1) – C(21)	107.0(1)	C(6) – C(7) – C(8)	113.4(3)
C(8) – S(1) – C(21)	103.1(1)	S(1) – C(8) – C(7)	111.1(2)
S(1) – C(1) – C(6)	109.9(2)		

(a) Estimated standard deviations in the least significant figure are given in parentheses.

The data exhibit interesting structural features of the 1-phenylbenzo[b]thiophenium perchlorate: the small angle of the C(1)-S(1)-C(8) and the short bond length of the S(1)-C(21) bond. The bonds around the sulfur are arranged pyramidally and the angles around the sulfur are 92.1, 103.1, and 107.0°. The bond length of the S(1)-C(21) is 1.784 Å and the ring S(1)-carbon bond lengths are 1.762 and 1.790 Å. The small bond angle of the C(1)-S(1)-C(8) is related to the five-membered ring and similar to those of 1,2,3,5-tetramethylbenzo[b]-thiophenium tetrafluoroborate (**10**) (92.2°)[1g] and 2-isobutyl-1,3-dihydrobenzo[c]thiophenium perchlorate (**11**) (95.7°).[14] The ring S-C bond lengths [S(1)-C(1) and S(1)-C(8)] are very close to those of the S-methyl analog **10** (1.768 and 1.779 Å, respectively).[1g] However, the S(1)-C(21) bond is short compared with the corresponding S-methyl bond (1.806 Å) in **10**. This short bond length may be characteristic of the sulfur-sp^2 carbon bond but the value is still in the range of the observed S-C(sp^3) bond (1.778 to 1.882 Å).[15]



(**10**)



(**11**)

The intermolecular contacts show a relatively short distance between the sulfur atom and the oxygen atom of the perchlorate anion. The distance between the S(1) and the O(2) atoms is 3.092 Å and is shorter than that of the sum of the van der Waals radii of sulfur and oxygen atoms (3.15 Å[15]). The bond angles of the O(2)-S(1)-C(n) (n = 1, 8, and 21) are 95.7, 77.7, and 157.1 °, respectively. Accordingly, these data indicate that there is some electrostatic interaction between the sulfonium center and the oxygen atom but no directional preference for a strong interaction.

In summary, we have established that various substituted 1-arylbenzo[b]thiophenium salts (**4**) are readily prepared by intramolecular cyclization of [*o*-(arylthio)phenyl]ethenes (**3**). This cyclization is strongly affected by the presence of the substituent on the double bond and the solvent polarity. Especially, the presence of the

substituent stabilizing the intermediate cation (**7**) promises to give 1-arylbenzo[b]thiophenium salts in high yields. The X-ray structural analysis of the 1-phenylbenzo[b]thiophenium perchlorate (**4b**: X = ClO_4) confirms the exact structure and indicates the short bond length of the S(1)-C(21) bond which is considered to be attributed to the stability of the 1-arylbenzo[b]thiophenium salts on the basis of the rules by Jones and Kirby et al.[16]

EXPERIMENTAL

Melting points were determined with a Yanaco micromelting point apparatus and are uncorrected. NMR spectra were taken with a Hitachi R 600, Bruker AC-250, or JEOL GSX 400. IR spectra were obtained with a Hitachi 270-30. Mass spectra were obtained with a Shimadzu GC-MS 7000. Elemental analyses were performed by the Service Center of the Elementary Analysis of Organic Compounds, Faculty of Science, Kyushu University.

*Preparation of [(o-Phenylthio)phenyl]ethenes (**3**).*

General Procedure.

To a solution of diphenyl sulfide (8.33 mL, 50 mmol) in THF (50 mL) was added dropwise n-BuLi (1.54 M in hexane, 38.9 mL, 60 mmol) at room temperature under N_2 atmosphere and the mixture was stirred for 4 h at room temperature. The mixture was cooled to - 70 °C and a solution of an appropriate ketone (50 mmol) in THF (20 mL) was added dropwise. The mixture was allowed to warm to room temperature, stirred for 12 h, and poured into water. The product was extracted with ether-benzene and purified by column chromatography on alumina (400 g) with ether-EtOH as eluent. The effluent was concentrated under reduced pressure to give crude 1-[2-(phenylthio)phenyl]-1-ethanol in 30-50% yield. The crude alcohol was used for dehydration without further purification because it contained the impurity which could not be separated completely by column chromatography on alumina and was in part dehydrated to olefin during workup. To a solution of the crude alcohol (ca 6 mmol) in ether (10 mL) and pyridine (0.96 mL, 12 mmol) was added $SOCl_2$ (0.52 mL, 7.2 mmol) at 0 °C. The mixture was stirred for 3 h, poured into water, and extracted with ether-benzene to give [(*o*-phenylthio)phenyl]ethenes (**3**) in 75-90% yield, which were purified further by column chromatography on alumina with CH_2Cl_2-hexane eluent.

*1-[2-(Phenylthio)phenyl]-1,2-diphenylethene (**3b**):* oil. ^{1}H NMR ($CDCl_3$, 60 MHz) δ 6.50-7.50 (m, =CH and ArH); MS m/z 364 (M^+, 78%), 286 (M^+ - PhH, 100). Anal. Calcd for $C_{26}H_{20}S$: C, 85.67; H, 5.53. Found: C, 85.61; H, 5.53.

*1-(4-Methoxyphenyl)-2-phenyl-1-[2-(phenylthio)phenyl]ethene (**3c**):* mp 62-63 °C (hexane-benzene). ^{1}HNMR ($CDCl_3$, 60 MHz) δ 3.74 (s, OMe), 6.72-7.35 (m, =CH and ArH); MS m/z 394 (M^+, 100%), 316 (M^+ - PhH, 93). Calcd for $C_{27}H_{22}OS$: C, 82.20; H, 5.62. Found: C, 82.07; H, 5.69.

*2-(4-Methoxyphenyl)-1-phenyl-1-[2-(phenylthio)phenyl]ethene (**3d**):* oil. ^{1}H NMR ($CDCl_3$, 60 MHz) δ 3.71 (s, OMe), 6.58-7.29 (m, =CH and ArH); MS m/z 394 (M^+, 100), 316 (M^+-PhH, 94). Calcd for $C_{27}H_{22}OS$: 82.20; H, 5.62. Found: C, 81.90; H, 5.68.

*1-Phenyl-1-[2-(phenylthio)phenyl]prop-1-ene (**3f**):* oil (a mixture of E and Z isomers, 74 : 26). ^{1}H NMR ($CDCl_3$, 250 MHz) δ 1.61 (d, *J* = 7, Me, minor), 1.85 (d, *J* = 7, Me, major), 5.80 (q, *J* = 7, =CH, major), 6.26 (q, *J* = 7, =CH, minor), 7.07-7.31 (m, ArH); MS m/z 302 (M^+, 70%), 287 (M^+ - Me, 27), 224 (M^+ - PhH, 100), 209 (224 - Me, 43). Calcd for $C_{21}H_{18}S$: C, 83.40; H, 6.00. Found: C, 83.44; H, 5.97.

*1-Phenyl-1-[2-(phenylthio)phenyl]ethene (**3g**):* oil. ^{1}HNMR ($CDCl_3$, 60 MHz) δ 5.15 (d, *J* = 1, =CH), 5.67 (d, *J* = 1, =CH), 7.00-7.15 (m, ArH); MS m/z 288 (M^+, 38%), 210 (M^+ - PhH, 100). Calcd for $C_{20}H_{16}S$: C, 83.29; H, 5.59. Found: C, 83.51; H, 5.51.

1-[5-Methyl-2-[(4-methylphenyl)thio]phenyl]]-1,2-diphenylethene (3a).

To a stirred mixture of bis(4-methylphenyl) sulfide (21.4 g, 0.1 mol), anhydrous aluminum chloride (20.0 g, 0.15 mol), and carbon disulfide (50 mL) was added dropwise benzoyl chloride (17.4 mL, 0.15 mol) at 0 °C. After the addition, the mixture was stirred for 4 h at 0 °C, poured onto ice, and extracted with ether-benzene. The organic layer was washed with water, 1 M NaOH, saturated NaCl, and dried. After evaporation of the solvent, the residue was passed through a column of alumina (500 g). Elution with benzene-ether gave *5-methyl-2-[(4-methylphenyl)thio]benzophenone* as an oil, 19.8 g (62 %). ^{1}HNMR ($CDCl_3$, 60 MHz) δ 2.29 (s, Me), 2.31 (s, Me), 6.39-7.87 (m, ArH); IR (neat) 1666 cm^{-1} (C=O). Calcd for $C_{21}H_{18}OS$: C, 79.21; H, 5.70. Found: C, 79.19; H, 5.60.

To a solution of benzylmagnesium chloride in ether prepared from Mg (0.72 g, 30 mmol), benzyl chloride (3.45 mL, 30 mmol), and anhydrous ether (60 mL) was added dropwise a solution of the preceding benzophenone (6.36 g, 20 mmol) in anhydrous ether (20 mL). The mixture was refluxed for 1 h and then quenched with aqueous HCl (2 M, 40 mL). An ether-benzene extract of the product was washed with water, saturated NaCl, dried, and evaporated. Column chromatography of the residue with alumina/benzene-EtOH gave *1-[5-methyl-2-[[(4-methylphenyl)thio]phenyl]-1,2-diphenylethanol*, 8.21 g (100 %), mp 92-93 °C (hexane-benzene). ^{1}HNMR (CCl_4, 60 MHz) δ 2.10 (s, Me), 2.20 (s, Me), 3.34 (d, J = 13, CH), 3.82 (d, J = 13, CH), 4.30 (s, OH, exchangeable with D_2O), 6.81-7.45 (m, ArH). Calcd for $C_{28}H_{26}OS$: C, 81.91; H, 6.38. Found: C, 81.74; H, 6.30.

A mixture of the triarylethanol prepared (6.0 g, 14.6 mmol) and 85% phosphoric acid (25 mL) was refluxed for 1.5 h and then quenched with cold water. An ether-benzene extract of the product was washed with water, saturated NaCl, and dried. Evaporation of the solvent gave *1-[5-methyl-2-[[(4-methylphenyl)thio]-phenyl]-1,2-diphenylethene (3a)* (5.10 g, 89%), mp 107-108 °C. ^{1}HNMR (CCl_4, 60 MHz) δ 2.20 (s, 2Me), 6.88-7.20 (m, =CH and ArH); MS m/z 392 (M^+, 100%), 300 (M^+ - TolH, 90). Calcd for $C_{28}H_{25}S$ requires C, 85.67; H, 6.16. Found: C, 85.29; H, 6.11.

1-Phenyl-2-[2-(phenylthio)phenyl]prop-1-ene (3e).

According to the procedure described for the preparation of ethene **3a**, propene **3d** was prepared by using *o*-(phenylthio)acetophenone[17] and benzylmagnesium chloride. Similar workup of the reaction gave *1-phenyl-2-[2-(phenylthio)phenyl]propan-2-ol* as an oil (91%). ^{1}HNMR ($CDCl_3$, 60 MHz) δ 1.66 (s, Me), 3.37 (s, CH_2 and OH), 7.00-7.48 (m, ArH). Calcd for $C_{21}H_{20}OS$: C, 78.71; H, 6.29. Found: C, 78.51; H, 6.32. Dehydration was performed in the procedure described in general procedure by using thionyl chloride-pyridine followed by column chromatography on alumina. *1-Phenyl-2-[2-(phenylthio)phenyl]prop-1-ene (3e)* was obtained as an oil (93%). ^{1}HNMR ($CDCl_3$, 60 MHz) δ 2.21 (d, J = 1, Me), 6.38 (q, J = 1, =CH), 7.10-7.27 (m, ArH); MS m/z 302 (M^+, 90%), 224 (M^+ - PhH, 100). Calcd for $C_{21}H_{18}S$: C, 83.40; H, 6.00. Found: C, 83.28; H, 5.93.

Preparation of 1-Arylbenzo[b]thiophenium Tribromides (4: X = Br_3) by Bromination of 1-[o-(phenylthio)phenyl]ethenes (3) with 2.2 Molar Amounts of Bromine.

General Procedure.

A solution of bromine (0.704 g, 4.4 mmol) in CH_2Cl_2 (10 mL) was added dropwise at 0 °C to a solution of [*o*-(phenylthio)phenyl]ethene **3** (2 mmol) in CH_2Cl_2 (40 mL) and the mixture was stirred for 1 h at 0 °C. After evaporation of the solvent, the resulting red-brown oil solidified on treatment with ether and the solid was filtered. Further purification was conducted by recrystallization from ether and CH_2Cl_2 (or EtOH).

5-Methyl-1-(4-methylphenyl)-2,3-diphenylbenzo[b]thiophenium Tribromide (4a: X = Br_3) (yield, 100%), amorphous solid. ^{1}HNMR ($CDCl_3$, 250 MHz) δ 2.33 (s, Me), 2.49 (s, Me), 7.15-7.80 (m, ArH), 8.30-8.50 (m, ArH); ^{13}CNMR ($CDCl_3$, 63 MHz) δ 22.63, 23.29, 119.37, 126.79, 128.54, 129.02, 129.94, 130.18, 130.29, 130.45, 130.61, 130.79, 131.64, 132.74, 133.07, 133.50, 137.09, 143.79, 146.03, 146.59, 146.88. An NMR spectroscopically pure **4a** (X = Br_3) was obtained by the above procedure but further

purification for analysis failed because of the partial decomposition.

*1,2,3-Triphenylbenzo[b]thiophenium Tribromide (**4b: X = Br_3**)* (yield, 100%); mp 154-155 °C. ^{1}HNMR ($CDCl_3$, 250 MHz) δ 7.21-7.92 (m, ArH), 8.35-8.58 (m, ArH); ^{13}CNMR ($CDCl_3$, 63 MHz) δ 122.53, 126.55, 127.55, 128.50, 129.39, 129.61, 129.70, 130.07, 130.25, 130.46, 130.70, 130.86, 131.22, 131.86, 132.02, 134.55, 135.44, 136.13, 143.26, 146.72. Calcd for $C_{26}H_{19}Br_3S$: C, 51.77; H, 3.18. Found: C, 52.12; H, 3.27.

*2-Methyl-1,3-diphenylbenzo[b]thiophenium Tribromide (**4f: X = Br_3**)* (yield, 30%), mp 134-136 °C. ^{1}HNMR ($CDCl_3$, 60 MHz) δ 2.39 (s, Me), 7.51-7.92 (m, ArH), 8.08-8.35 (m, ArH). Calcd for $C_{21}H_{17}Br_3S$: C, 46.61; H, 3.17. Found: C, 46.35; H, 3.16.

*Reaction of **4b (X = Br_3)** with 1,1-Diphenylethene.*

In an NMR tube **4b** (X = Br_3) (90 mg, 0.15 mmol) was mixed with 1,1-diphenylethene (36 mg, 0.20 mmol) in $CDCl_3$ (0.5 mL). The NMR spectrum showed that 1,1-diphenylethane [δ 5.42 (s, $=CH_2$)] was converted to 1,2-dibromo-1,1-diphenylethane [δ 4.47 (s, CH_2Br)] which was identified by comparison with the authentic sample prepared independently by the reaction of 1,1-diphenylethene with bromine in CCl_4. Benzo[b]thiophenium bromide **4b** (X = Br) was obtained by column chromatography on alumina with EtOH eluent.

Conversion of tribromide **4b** (X = Br_3) into **4b** (X = Br) was almost quantitatively achieved by passing through a column of alumina with EtOH as the eluent or by refluxing in EtOH. The higher melting point and the chemical shifts of low magnetic field at δ 9.05-9.35 are characteristic of **4b** (X = Br).

*1,2,3-Triphenylbenzo[b]thiophenium Bromide (**4b: X = Br**):* mp 238-240 °C. ^{1}HNMR ($CDCl_3$, 250 MHz) δ 7.20-8.12 (m, ArH), 9.05-9.35 (m, ArH); ^{13}CNMR ($CDCl_3$, 63 MHz) δ 123.81, 126.55, 126.94, 129.01, 129.22, 129.56, 129.85, 130.20, 130.29, 130.38, 130.61, 130.98, 131.27, 132.77, 133.90, 134.55, 136.67, 143.11, 146.02. Calcd for $C_{21}H_{17}BrS$: C, 66.15; H, 4.49. Found: C, 65.87; H, 4.35.

*Preparation of 1-Arylbenzo[b]thiophenium Bromides (**4: X = Br**) by Bromination of [o-(Arylthio)phenyl]-ethenes (**3**).*

General Procedure.

To a solution of [*o*-(arylthio)phenyl]ethene (**3**) (1.0 g) in a solvent (100-110 mL) was added a solution of 1.1 molar amounts of bromine in the same solvent (20-30 mL) at 0 °C and the mixture was stirred for 1 h at 0 °C. The solvent was evaporated and the products were extracted with CH_2Cl_2. The CH_2Cl_2 extract was washed with saturated $NaHCO_3$ and saturated NaCl. After evaporation of the solvent the products were separated by column chromatography on alumina. Elution with hexane-CH_2Cl_2 gave 1-[2-(arylthio)phenyl]-2-bromoethene **5**. Elution with CH_2Cl_2-EtOH gave 1-arylbenzo[b]thiophenium bromide **4** (X = Br). In the case of the bromination in AcOH the reaction was carried out at a room temperature. The results are given in Table 1.

When **3a** or **3b** was treated with 2.2 molar amounts of bromine in CH_2Cl_2 as described above, 1-arylbenzo[b]thiophenium bromide **4a** (X = Br) or **4b** (X = Br), respectively, was obtained quantitatively after column chromatography on alumina. Since some benzo[b]thiophenium bromides **4** (X = Br) were not satisfied with the combustion analysis because of the amorphous or hygroscopic nature, these analyses were carried out after conversion to the corresponding tetrafluoroborate or perchlorate according to the procedure for **4b: X = ClO_4**.

*5-Methyl-1-(4-methylphenyl)-2,3-diphenylbenzo[b]thiophenium Bromide (**4a: X = Br**):* amorphous solids. ^{1}HNMR ($CDCl_3$, 250 MHz) δ 2.31 (s, Me), 2.46 (s, Me), 7.05-7.97 (m, ArH), 8.79-8.95 (m, ArH); ^{13}CNMR ($CDCl_3$, 63 MHz) δ 21.70, 21.99, 120.25, 127.12, 127.27, 129.19, 129.34, 129.72, 129.80, 130.06, 130.27, 130.41, 130.71, 131.03, 131.68, 132.12, 137.36, 143.39, 145.25, 145.90, 146.09. *Tetrafluoroborate* (**4a: X = BF_4**): mp 201.5-202.5 °C (CH_2Cl_2-ether). ^{1}HNMR (CD_3CN, 60 MHz) δ 2.35 (s, Me), 2.49 (s, Me), 7.18-7.70 (m, ArH), 7.89-8.02 (m, ArH). Calcd for $C_{28}H_{23}BF_4S$: C, 70.06; H, 4.84. Found: C, 70.31; H, 4.85.

*3-(4-Methoxyphenyl)-1,2-diphenylbenzo[b]thiophenium Bromide (**4c: X = Br**):* hygroscopic crystals; ^{1}HNMR ($CDCl_3$, 250 MHz) δ 3.86 (s, OMe), 6.92-8.18 (m, ArH) and 8.79-8.92 (m, ArH); ^{13}CNMR ($CDCl_3$, 63 MHz) δ 55.50, 115.13, 122.30, 124.32, 126.55, 127.47, 129.36, 129.98, 130.32, 130.72, 131.20, 131.24, 133.07, 133.82, 134.45, 135.64, 143.16, 145.90, 161.05.

*2-(4-Methoxyphenyl)-1,3-diphenylbenzo[b]thiophenium Bromide (**4d: X = Br**):* hygroscopic crystals; ^{1}HNMR ($CDCl_3$, 250 MHz) δ 3.71 (s, OMe), 6.57-7.98 (m, ArH), 8.87-8.99 (m, ArH); ^{13}CNMR ($CDCl_3$, 250 MHz) δ 55.39, 114.92, 119.23, 124.57, 126.13, 129.16, 129.71, 130.14, 130.40, 130.65, 130.90, 131.21, 131.27, 131.56, 132.78, 133.82, 134.43, 137.22, 143.55, 143.99, 161.14.

*3-Methyl-1,2-diphenylbenzo[b]thiophenium Bromide (**4e: X = Br**):* mp 129-139 °C (hygroscopic); δ_H (250 MHz, $CDCl_3$) 2.62 (s, Me), 7.34-7.93 (m, ArH) and 8.85-8.87 (m, ArH); δ_C (63 MHz, $CDCl_3$) 14.09, 123.98, 125.32, 127.14, 129.63, 129.74, 130.04, 130.72, 131.10, 131.28, 132.89, 134.14, 134.56, 135.38, 143.61 and 144.05. *Perchlorate* (**4e: X = ClO_4**): mp 192-196 °C (CH_2Cl_2-CCl_4). Calcd for $C_{21}H_{17}ClO_4S$: C, 62.92; H, 4.27. Found: C, 62.72; H, 4.25.

*2-Methyl-1,3-diphenylbenzo[b]thiophenium Bromide (**4f: X = Br**):* mp 187-188 °C (ether-CH_2Cl_2). ^{1}HNMR ($CDCl_3$, 250 MHz) δ 2.35 (s, Me), 7.20-8.15 (m, ArH), 8.73-8.83 (m, ArH); ^{13}CNMR ($CDCl_3$, 63 MHz) δ 12.91, 123.68, 125.84, 128.34, 129.59, 129.79, 130.12, 130.56, 131.38, 131.66, 133.01, 133.74, 134.12, 134.86, 142.90, 147.82. Calcd for $C_{21}H_{17}BrS$: C, 66.15; H, 4.49. Found: C, 65.87; H, 4.35.

*1,3-Diphenylbenzo[b]thiophenium Bromide (**4g: X = Br**):* mp 213.5-215.5 °C. ^{1}HNMR ($CDCl_3$, 250 MHz) δ 7.30-8.15 (m, ArH and CH), 8.48-8.53 (m, ArH); ^{13}CNMR ($CDCl_3$, 63 MHz) δ 121.92, 124.97, 126.58, 128.32, 128.64, 129.36, 130.62, 130.76, 131.10, 133.23, 134.13, 135.67, 140.10, 153.92. Calcd for $C_{20}H_{15}BrS$: C, 65.40; H, 4.12. Found: C, 65.62; H, 4.23.

*1-Bromo-2-(4-methoxyphenyl)-1-phenyl-2-[2-(phenylthio)phenyl]ethene (**5c**):* oil. ^{1}HNMR ($CDCl_3$, 60 MHz; a 30:70 isomeric mixture) δ 3.56 (s, OMe, major), 3.67 (s, OMe, minor), 6.37-7.47 (m, ArH); MS m/z 392 (M^+-Br, 100%, 315 (M^+-Br-Ph, 71). Calcd for $C_{27}H_{21}BrOS$: C, 68.50; H, 4.47. Found: C, 68.65; H, 4.60.

*2-Bromo-1-phenyl-1-[2-(phenylthio)phenyl]prop-1-ene (**5f**):* mp 90-91 °C. ^{1}HNMR ($CDCl_3$, 60 MHz; a 28:72 isomeric mixture) δ 2.23 (s, Me, major), 2.46 (s, Me, minor), 6.61-7.75 (m, ArH); MS m/z 382 (M^+ + 2, 2%), 380 (M^+, 2), 301 (M^+ - Br, 100), 286 (301 - Me, 37). Calcd for $C_{21}H_{17}BrS$: C, 66.15; H, 4.49. Found: C, 66.03; H, 4.50.

*2-Bromo-1-phenyl-1-[2-(phenylthio)phenyl]ethene (**5g**):* mp 109-110 °C. ^{1}HNMR ($CDCl_3$, 60 MHz; a 25:75 isomeric mixture) δ 6.44 (s, =CH, minor), 6.82 (s, =CH, major), 6.92-7.58 (m, ArH); MS m/z 368 (M^+ + 2, 10%) 366 (M^+, 10); 287 (M^+ - Br, 100). Calcd for $C_{20}H_{15}BrS$: C, 65.40; H, 4.12. Found: C, 65.46; H, 4.23.

*Reaction of [2-(Phenylthio)phenyl]ethenes (**3f** and **3g**) with Iodine Monochloride (ICl).*

To a solution of [*o*-(phenylthio)phenyl]ethene (**3f** or **3g**) (2 mmol) in CH_2Cl_2 (50 mL) was added dropwise at 0 °C a solution of ICl (490 mg, 3 mmol) in CH_2Cl_2 (10 mL) and the mixture was stirred for 5 h at 0 °C. Aqueous $Na_2S_2O_3$ was added and the CH_2Cl_2 layer was separated and washed with water. After evaporation of the solvent the residue was submitted to column chromatography on alumina. After elution with CH_2Cl_2 the product was collected with CH_2Cl_2-EtOH as the eluent and concentrated. $AgClO_4$ (500 mg) and MeCN (20 mL) was added and stirred for 12 h at a room temperature. The mixture was passed through a column of alumina with CH_2Cl_2-EtOH eluent. The solvent was evaporated and crystallized by adding ether.

*2-Methyl-1,3-diphenylbenzo[b]thiophenium Perchlorate (**4f: X = ClO_4**):* mp 193-195 °C. ^{1}HNMR ($CDCl_3$-DMSO-d_6, 250 MHz) δ 2.29 (s, Me), 7.53-7.84 (m, ArH), 8.22-8.25 (m, ArH); ^{13}CNMR ($CDCl_3$-DMSO-d_6, 63 MHz) δ 12.30, 122.78, 126.18, 127.98, 128.85, 129.31, 129.76, 130.14, 130.37, 130.64, 131.80, 132.24, 133.20, 133.96, 135.19, 142.70, 147.91. Calcd for $C_{21}H_{17}ClO_4S$: C, 62.92; H, 4.27. Found: C, 62.68; H, 4.33.

*1,3-Diphenylbenzo[b]thiophenium Perchlorate (**4g: X = ClO_4**):* mp 168-170 °C. ^{1}HNMR ($CDCl_3$-DMSO-d_6, 250 MHz) δ 7.62-7.99 (m, ArH), 8.26-8.29 (m, ArH); ^{13}CNMR ($CDCl_3$-DMSO-d_6, 63 MHz) δ

118.93, 124.55, 126.78, 128.02, 128.40, 129.31, 130.10, 130.60, 130.98, 131.16, 131.29, 133.50, 134.47, 135.51, 139.64, 155.12. Calcd for $C_{20}H_{15}ClO_4S$: C, 62.10; H, 3.91. Found: C, 61.51; H, 3.89.

*Preparation of 1,2,3-Triphenylbenzo[b]thiophenium Perchlorate (**4b**: X = ClO_4).*

A solution of 1,2,3-triphenylbenzo[b]thiophenium bromide (**4b**: X = **Br**) (2.00 mmol) in MeCN (50 mL) was refluxed for 12 h in the presence of silver perchlorate (2.50 mmol). After removal of the resulting silver bromide, the filtrate was concentrated and the residue was submitted to column chromatography on alumina. Elution with EtOH gave an oil which was crystallized from CCl_4, yielding white crystals of **4b** (X = ClO_4) (1.82 mmol, 91%). Mp 216-219 ^oC (CH_2Cl_2-CCl_4). Calcd for $C_{26}H_{19}ClO_4S$: C, 67.46; H. 4.14. Found: C, 67.27; H, 4.15. A suitable single crystal of **4b** (X = ClO_4) was obtained by a slow evaporation of the solution of **4b** (X = ClO_4) in CCl_4-CH_2Cl_2.

*Crystal Data of **4b** (X = ClO_4)*

$C_{26}H_{19}ClO_4S$, M = 462.95. Monoclinic, a = 10.612 (1), b = 17.058 (1), c = 12.285 (1) Å, β = 92.098 (8)^o, V = 2222.4 (3) Å^3, space group *P* $2_1/n$ (#14), Z = 4, D_{calc} = 1.384 g/cm^3. Colorless, prismatic crystals. Crystal dimensions: 0.300 x 0.300 x 0.300 mm, $\mu_{(CuK\alpha)}$ = 26.50 cm^{-1}.

Data Collection , Structure Solution, and Refinement

A colorless prismatic crystal of **4b** (X = ClO_4) was mounted on a glass fiber. All measurements were made on a Rigaku AFC5R diffractomer with graphite monochromated Cu Kα radiation (λ = 1.54178 Å) and a 12KW rotating anode generator.

Cell constants and an orientation matrix obtained from a least-squares refinement using the setting angles of 25 carefully centered reflections in the range $55.78 < 2\theta < 56.88^o$ corresponded to a monoclinic cell with dimensions given above. For Z = 4 and F.W. = 462.95, the calculated density is 1.384 g/cm^3 and the space group was determined to be: $P2_1/n$ (# 14).

The data were collected at a temperature of 23 ± 1 ^oC using the ω-2θ scan technique to a maximum 2θ value of 120.0^o. The data were corrected for Lorentz and polarization effects. The structure was solved by direct methods. The non-hydrogen atoms were refined anisotropically. The final cycle of full-matrix least-squares refinement was based on 2451 observed reflections ($I > 3.00\sigma(I)$) and 290 variable parameters and converged with unweighted and weighted agreement factors of: $R = \Sigma \, | \, |Fo| - |Fc| \, | \, / \, \Sigma \, |Fo| = 0.047$, $R = [(\Sigma \, w \, (|Fo| - |Fc|)^2 \, / \, \Sigma \, w \, Fo^2)]^{1/2} = 0.068$. All calculation were performed using the TEXSAN[18] crystallographic software package of Molecular Structure Corporation.

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