

A drastic effect of halide anions on the nucleophilic substitution of 1-phenylbenzo[*b*]thiophenium salts

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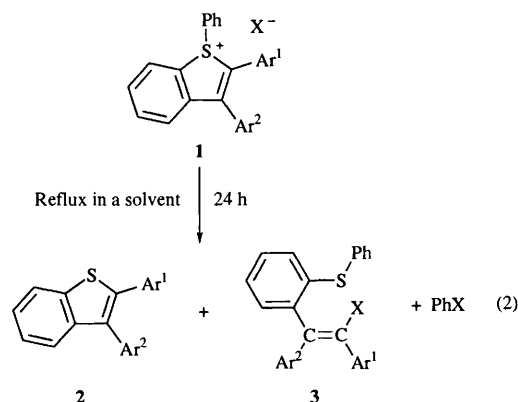
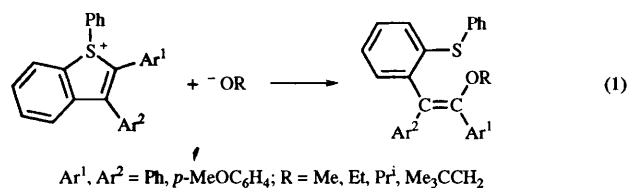
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Nucleophilic substitution of 1,2,3-triarylbenzo[*b*]thiophenium salts with halide anions (Cl⁻ and Br⁻) has been found to yield 2,3-diarylbenzo[*b*]thiophenes, haloethenes and 1,2-diaryl-1-halo-2-[2-(phenylsulfanyl)phenyl]ethenes and especially the reaction with iodide anion gives only 2,3-diarylbenzo[*b*]thiophenes and iodobenzene, indicating that halide anions behave quite differently from the reaction with alkoxide anions reported previously.

1-Phenylbenzo[*b*]thiophenium salts have unique structural features¹ and are expected to show interesting chemical properties. The short, strong Ph-S⁺ bond resists nucleophilic cleavage in the reaction with nucleophiles and favours the ring-opening of the thiophene ring. Previously we have reported that the reaction of 1,2,3-triarylbenzo[*b*]thiophenium salts with alkoxide anion undergoes a nucleophilic ring-opening reaction and gives exclusively 1-alkoxy-1,2-diaryl-2-[2-(phenylsulfanyl)phenyl]ethenes [reaction (1)].² The stereochemistry of the ring-opened products, alkoxyethenes, is the *Z* configuration which implies that the ring-opening reaction proceeds with the complete retention of configuration. On the basis of the stereochemical outcome we have proposed two possible mechanisms: a mechanism involving nucleophilic substitution *via* σ -sulfuranes and a rapid addition-elimination mechanism for the ring-opening reaction.

In order to gain further information of the chemical behaviour toward nucleophiles, we have studied the nucleophilic reaction of 1,2,3-triarylbenzo[*b*]thiophenium salts with halide anions. Surprisingly, the reaction with the iodide anion caused exclusive bond breaking of the 1-phenylbenzo[*b*]thiophenium salts. Other halide anions also favoured the cleavage of the Ph-S⁺ bond rather than the ring-opening reaction. In this communication, we report the interesting drastic behaviour of halide anions in the nucleophilic reaction of 1,2,3-triarylbenzo[*b*]thiophenium salts.

Substituted 1-phenylbenzo[*b*]thiophenium salts **1** were prepared by halogenation of the corresponding [2-(phenylsulfanyl)phenyl]alkenes.^{1a-3} The reactions of 1,2,3-triarylbenzo[*b*]thiophenium salts with halide anions were conducted by the thermal decomposition of the 1,2,3-triarylbenzo[*b*]thiophenium halides **1** (X = Br, Cl) and by the reaction of 1,2,3-triarylbenzo[*b*]thiophenium perchlorates **1** (X = ClO₄) with tetrabutylammonium iodide (Bu₄NI). A typical reaction is as follows. A suspension of 1,2,3-triphenylbenzo[*b*]thiophenium bromide **1a** (X = Br) in toluene was refluxed for 24 h. After removal of the toluene, 2,3-diphenylbenzo[*b*]thiophene **2a** (72%) and 1-bromo-1,2-diphenyl-2-[2-(phenylsulfanyl)phenyl]ethene **3a** (X = Br) (24%) were isolated by column chromatography on silica gel. The volatile product, bromobenzene (56%), was analysed by GC before column chromatography. Other 1,2,3-triarylbenzo[*b*]thiophenium halides **1** (X = Br and Cl) were decomposed by a similar manner. The reactions with the iodide anion were conducted by heating a mixture of triarylbenzo[*b*]thiophenium perchlorates and Bu₄NI in propionitrile. The conversion was low but no iodoethene **3** (X = I) was detected. The results are given in Table 1.



a: Ar¹ = Ar² = Ph; b: Ar¹ = *p*-MeOC₆H₄, Ar² = Ph;
c: Ar¹ = Ph, Ar² = *p*-MeOC₆H₄; d: Ar¹ = Ar² = *p*-MeOC₆H₄

The formation of benzo[*b*]thiophenes **2**, haloethenes **3** (X = Cl, Br, I) and haloethene indicates that competition between the breaking of the Ph-S⁺ bond and the C-S⁺ bond of the thiophene ring takes place during the nucleophilic substitution. Of particular note is the reaction of 1,2,3-triarylbenzo[*b*]thiophenium salts with Bu₄NI in which only bond cleavage of the Ph-S⁺ bond occurs. This result is quite different from the reaction with alkoxide anions where exclusive ring-opening reactions are observed.

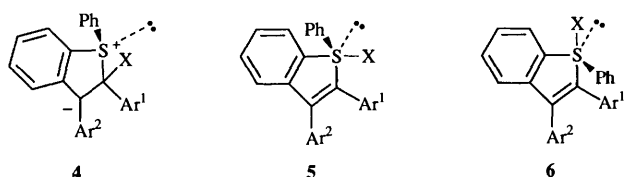
The formation of haloethenes **3** is highly stereoselective. Namely, only one isomer of the two possible *E*- and *Z*-configurations was present. It was, however, difficult to determine the configuration of the haloethenes **3** by spectral means. Finally, the absolute structure was analysed by a single crystal X-ray diffraction of (*Z*)-1-bromo-1-(4-methoxyphenyl)-2-phenyl-2-[2-(phenylsulfanyl)phenyl]ethene **3b** (X = Br).⁴

The reaction of 1-phenylbenzo[*b*]thiophenium salts **1** with halide anions involves bond cleavage of two types of S⁺-C bonds: the phenyl-S⁺ bond and the S⁺-C bond of the thiophene ring. From the crystal data^{1a} of 1,2,3-triphenylbenzo-

Table 1 Reaction of 1,2,3-triarylbenzo[*b*]thiophenium salts **1** with halide anions

	1			Reaction conditions	Yields of products (%) ^a			Product ratio [2]:[3]
	Ar ¹	Ar ²	X		2	3	PhX ^b	
a	Ph	Ph	Cl	Toluene, 110 °C	48	47 (X = Cl)	<i>c</i>	51:49
a	Ph	Ph	Br	Toluene, 110 °C	72	24 (X = Br)	56 (X = Br)	75:25
b	<i>p</i> -MeOC ₆ H ₄	Ph	Br	Toluene, 110 °C	55	34 (X = Br)	<i>c</i>	62:38
c	Ph	<i>p</i> -MeOC ₆ H ₄	Br	Toluene, 110 °C	78	17 (X = Br)	<i>c</i>	82:18
d	<i>p</i> -MeOC ₆ H ₄	<i>p</i> -MeOC ₆ H ₄	Br	Toluene, 110 °C	69	19 (X = Br)	<i>c</i>	78:22
a	Ph	Ph	ClO ₄	Bu ₄ NI, EtCN, 110 °C ^d	42	0	34 (X = I)	100:0
b	<i>p</i> -MeOC ₆ H ₄	Ph	ClO ₄	Bu ₄ NI, EtCN, 97 °C ^d	25	0	33 (X = I)	100:0
a	Ph	Ph	Br	NaOMe, MeOH, 64.5 °C ^e	0	100 (X = MeO)	0	0:100
b	<i>p</i> -MeOC ₆ H ₄	Ph	ClO ₄	NaOMe, MeOH, 64.5 °C ^e	0	100 (X = MeO)	0	0:100

^a Isolated yields by column chromatography on silica gel. ^b Determined by GC. ^c Not determined. ^d Reactions were not completed. ^e Ref. 2.



[*b*]thiophenium perchlorate **1a** (X = ClO₄), the Ph-S⁺ bond length is short (1.784 Å) and comparable to the ring S⁺-C bond length (1.790 Å). Accordingly, the ring S⁺-C bond is expected to be weak compared with the phenyl-S⁺ bonds and to undergo a nucleophilic bond fission. However, the choice of the bond fission is strongly dependent upon the nature of nucleophiles.

Addition-elimination is a generally accepted mechanism for nucleophilic substitution of unsaturated systems.⁵ The present reaction may proceed with the competing vinylic and aromatic addition-elimination processes yielding benzo[*b*]thiophenes **2** and ring-opened haloethenes **3**. The stereochemical outcome of the ring-opened haloalkenes suggests a rapid addition-elimination process *via* a short-lived intermediate **4** as reviewed by Rappoport,^{5b} where the stereochemistry of the product is retained and the *Z* isomer is formed.

On the other hand, the mechanisms involving a ligand-ligand coupling⁶ *via* σ -sulfuranes have been proposed in the reactions of triarylsulfonium ions⁷ and diaryl and alkyl aryl sulfoxides⁶ with organo-lithium and -magnesium reagents. Recently Furukawa and co-workers have isolated a stable σ -sulfuranium and analysed it by X-ray diffraction.⁸ Therefore, we postulate the formation of σ -sulfuranes **5** and **6** as the intermediates in the thermal decomposition, although it is not certain at the present time whether such a ligand coupling process proceeds *via* a concerted process or a rapid addition-elimination mechanism.

In summary, we have found a drastic element effect on the nucleophilic substitution of 1,2,3-triarylbenzo[*b*]thiophenium salts. The nucleophilic reaction with halide anions indicates that the dephenylation and ring-opening reactions are in competition and the ring-opening reaction proceeds with the retention of the configuration. In particular, the reaction with the iodide anion is an extreme example in which the dephenylation reaction only takes place. Such competing processes do not take place in the reaction with alkoxide anions. The differences between these

reactions may be attributed to the property of the counter anion (nucleophilic reagent). Detailed mechanistic studies of this interesting behaviour are now in progress.

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