ARYLTHIOSULFONIUM SALTS AS TRANSFER AGENTS OF THE S-ARYL GROUP TO DOUBLE BONDS

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The preparation of arylthioalkyl derivatives by the Ad_E reaction with alkenes is usually performed using covalent ArS–Y reagents (where Y is a halogen [1] or thiocyanogen [2]) or cationoids which are conventionally written as ArS^+Y^- (where Y^- is a non-nucleophilic counter-ion such as BF_4^- [3]). In the former case, the reaction products are β-halo or β-thiocyanide derivatives,* while in the latter, episulfonium salts are obtained which, upon further treatment with nucleophiles (Nu), form β-Nu-substituted arylthioethers. This latter variant is most promising as a preparative procedure, although its common use is hindered by difficulties related to the instability of the ArS^+Y^- cationoid generated in situ. We should note that there are no data on the structure of these reagents, while analogous systems for transfer of the MeS^+ have a complex composition and virtually do not contain the monomeric MeS^+Y^- salt [4].

It is clearly simpler to use reagents in which the ArS^+ group is stabilized as a stoichiometric ArSZ complex, where Z is a good leaving group. We have previously shown that diaryl disulfides may be such "stabilizers" [5] and that $[ArS(SAr)_2]^+Y^-$ reagents indeed are active transfer agents for the ArS^+ group in reactions with alkenes. However, the requirement of using stoichiometric quantities of $(ArS)_2$ as a "ballast" in these reactions produces certain difficulties. Thus, in the present work, we studied the possibility of using some sulfides as stabilizers for the ArS^+ group.

The reaction of aromatic sulfene chlorides (Ia-f) with Lewis acids $SbCl_5$ or SbF_5 in the presence of sulfides (II)-(V) at −30°C to −50°C readily yields the corresponding arylthiosulfonium salts (VI)-(IX) by the following general scheme:

$$\underset{\text{(I)}}{ArSCl} + \underset{\text{(II)–(V)}}{SbCl_5(SbF_5) + R^1SR} \xrightarrow[\text{liquid } SO_2]{CH_2Cl_2 \text{ or}} \underset{\text{(VI)–(IX)}}{ArS\overset{+}{S}\begin{matrix}R\\ \diagup\\ \diagdown\\ R^1\end{matrix}} \; SbCl_6^-(SbF_5Cl^-)$$

(I): Ar = Ph (a), 4-MeC_6H_4 (b), 4-ClC_6H_4 (c), 2,4,6-$Me_3C_6H_2$ (d), 4-$CF_3C_6H_4$ (e), C_6F_5 (f).

R = R^1 = Me (II); R = R^1 = $-(CH_2)_4-$ (III); R = Me, R^1 = 4-ClC_6H_4 (IV); R = R^1 = Ph (V).

(VI): R = R^1 = Me, Ar = Ph (a), 4-MeC_6H_4 (b), 4-ClC_6H_4 (c), 2,4,6-$Me_3C_6H_2$ (d), 4-$CF_3C_6H_4$ (e), C_6F_5 (f).

(VII): R = R^1 = $-(CH_2)_4-$, Ar = 4-ClC_6H_4 (a), 2,4,6-$Me_3C_6H_2$ (b).

(VIII): R = Me, R′ = 4-ClC_6H_4, Ar = Ph (a), 4-MeC_6H_4 (b), 4-ClC_6H_4 (c), 2,4,6-$Me_3C_6H_2$ (d), 4-$CF_3C_6H_4$ (e), C_6F_5 (f).

(IX): R = R^1 = Ph, Ar = Ph (a), 4-MeC_6H_4 (b), 4-ClC_6H_4 (c), 4-$MeOC_6H_4$ (d).

Salts (VI) and (VII) are rather stable in solid form and are characterized by the data in Table 1. Table 2 gives the PMR spectra of salts (VIII) which are stable only in solution. Salts (VI), (VIII), and (IX) were characterized by their ^{13}C NMR spectra. Analysis of the results obtained shows that these compounds are indeed sulfonium salts. The ^{13}C NMR spectra of salts (VI), (VIII), and (IX) will be discussed in a separate communication.

The salts obtained (VI)-(IX) are efficient transfer agents for the ArS^+ group in Ad_E reactions with cyclohexene (X), 1-methylcyclohexene (XI), tetramethylethylene (XII), cyclooctene (XIII), styrene (XIV), and isoprene (XV). In all cases, the reaction proceeds rather readily even at −10 to −30°C and, depending on the nature of

*A special case is the Ad_E reaction of covalent reagents under doping addition conditions giving various solvoadducts [3].

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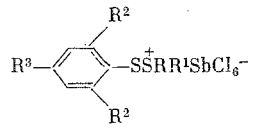
TABLE 1. Analytical and Spectral Data for Arylthiosulfonium Salts (VI) and (VII)



Salt	R	R^1	R^2	R^3	Yield, %	mp, °C	Found/calculated, % C	Found/calculated, % H	PMR spectra (δ, ppm)* for $\overset{+}{S}SR^1$
(VIa)	Me	Me	H	H	90	95–97	18,32 / 19,00	2,22 / 2,00	2,95 s (6H)
(VIb)	Me	Me	H	Me	92	92–95	19,91 / 20,80	2,47 / 2,52	2,94 s (6H)
(VIc)	Me	Me	H	Cl	95	97–99	17,88 / 17,79	1,86 / 1,87	2,95 s (6H)
(VId)	Me	Me	Me	Me	92	123–125	–	–	3,12 s (6H)
(VIe)	Me	Me	H	CF_3	90	85–87	–	–	2,97 s (6H)
(VIf)	Me	Me	†		93	94–96	–	–	3,16 s (6H)
(VIIa)	$-(CH_2)_4-$		H	Cl	85	85–87	20,55 / 21,18	2,17 / 2,12	2,30 m (4H), 3,75 m (4H)
(VIIb)	$-(CH_2)_4-$		Me	Me	93	100–104	26,88 / 27,00	3,30 / 3,30	2,8 m (4H), 3,85 m (4H)

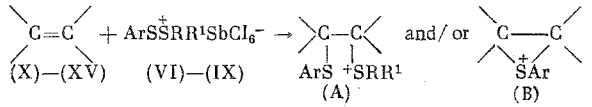
*The aromatic proton signals are at 7.00–7.80 ppm and the benzene ring methyl protons are at 2.38–2.40 ppm (for R^3=Me) and 2.25–2.60 ppm (for $R^2=R^3$=Me).
†ArS = C_6F_5S.

TABLE 2. PMR Spectral Data for Salts (VIII) $ArS\overset{+}{S}-C_6H_4Cl$ (Me)

Salt	Ar	PMR spectrum (δ, ppm)* for $Me\overset{+}{S}$	Salt	Ar	PMR spectrum (δ, ppm)* for $Me\overset{+}{S}$
(VIIIa)	Ph	3,33 s	(VIIIг)	2,4,6-$Me_3C_6H_2$	3,33 s
(VIIIb)	4-MeC_6H_4	3,26 s	(VIIIд)	4-$CF_3C_6H_4$	3,30 s
(VIIIc)	4-ClC_6H_4	3,29 s	(VIIIe)	C_6F_5	3,45 s

*See footnote in Table 1.

the alkene and/or reagent, leads to the formation of β-arylthiosulfonium salts (A) and/or S-arylepisulfonium salts (B) by the following scheme:



The reaction of alkenes with arylthiodialkylsulfonium salts (VI) and (VII) proceeds most unequivocally. In reactions with alkenes (X), (XIII), (XIV), and (XV), we found the exclusive formation of β-arylthioalkylsulfonium salts (A) (XVI)-(XXVII) which are readily separated as compounds which are rather stable as solids. Their structure is supported by the data in Table 3. We should however note that salts (XIX), (XXIIIa,b), and (XXVa,b) obtained from isoprene (XV) are 1,4-adducts (as shown by the PMR spectra) and mixtures of Z- and E-isomers (the presence of the triplet of the $C=CHCH_2$ fragment at 5.35 ppm (1H) and of two broad singlets of the MeC=C fragment is diagnostic). However, PMR study of the reaction of (XV) with (VIc) and (VIIa) showed that 1,2-adducts are formed initially which later are readily converted to the more stable 1,4-adducts

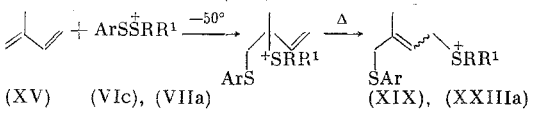
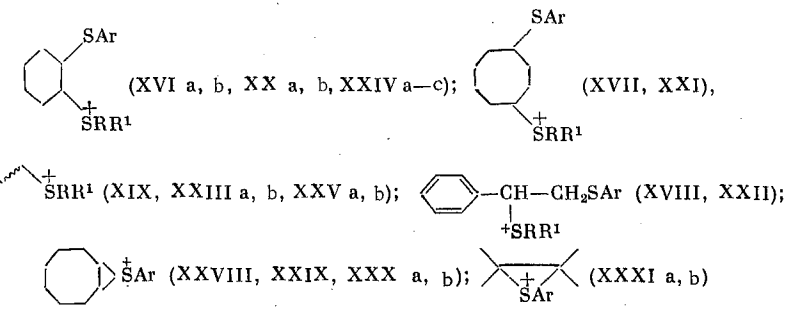


TABLE 3. Analytical and Spectral Data for β-Arylthioalkylsulfonium and S-Arylepisulfonium Salts:



Salt	Ar	R	R¹	Yield, %	mp, °C	Found/calculated, %		PMR spectrum (δ, ppm)*
						C	H	
(XVIa)	4-MeC_6H_4	Me	Me	94	–	–	–	2,73 s (3H), 2,88 s (3H), 3,47 m (2H)
(XVIb)	4-ClC_6H_4	Me	Me	85	–	28,93 27,02	3,75 3,25	2,72 s (3H), 2,85 s (3H), 3,42 m (2H)
(XXa)	4-ClC_6H_4	$-(CH_2)_4-$		83	101–103	29,80 29,64	3,27 3,43	2,25 m (4H), 2,92 m (2H), 3,42 m (4H)
(XXb)	2,4,6-$Me_3C_6H_2$	$-(CH_2)_4-$		96	117–120	34,27 34,78	4,31 4,46	2,33 m (4H), 3,53 m (6H)
(XXIVa)	4-MeC_6H_4	Me	4-ClC_6H_4	92	30–35	35,58 34,39	4,27 3,47	3,20 m (3H), 3,48 m (2H)
(XXIVb)	4-ClC_6H_4	Me	4-ClC_6H_4	90	30–32	32,75 31,74	3,32 2,95	3,22 m (3H), 3,48 m (2H)
(XXIVc)	2,4,6-$Me_3C_6H_2$	Me	4-ClC_6H_4	83	25–30	36,80 36,37	4,66 3,89	3,30 m (3H), 3,55 m (2H)
(XVII)	4-ClC_6H_4	Me	Me	88		29,50 29,54	3,97 3,73	2,70 s (3H), 2,88 s (3H), 3,65 m (2H)

TABLE 3 (continued)

Salt	Ar	R	R¹	Yield, %	mp, °C	Found/calculated, % C	Found/calculated, % H	PMR spectrum (δ, ppm)*
(XXI)	4-ClC_6H_4	$-(CH_2)_4-$		88	–	30,07 31,96	3,44 3,88	2,27m (4H), 3,62 m (6H)
(XIX)	4-ClC_6H_4	Me	Me	83	–	24,80 25,67	3,10 2,99	1,95s (3H), 2,55 s (3H), 3,68m (4H), 5,35 t (1H)
(XXIIIa)	4-ClC_6H_4	$-(CH_2)_4-$		94	91–93	–	–	1,68 s (3H), 2,25m (4H), 2,92 m (2H), 3,42 m(4H), 5,35 t (1H)
(XXIIIb)	2,4,6-$Me_3C_6H_2$	$-(CH_2)_4-$		86	81–84	33,92 33,67	4,33 4,24	2,00 s (3H), 2,32m (4H), 3,25 m (8H), 3,37 s (2H), 5,35 t (1H)
(XXVa)	4-MeC_6H_4	Me	4-ClC_6H_4	93	41–44	33,32 33,34	3,45 3,25	1,68 s (3H), 3,08 s (3H), 3,60 s (2H), 4,18 m (2H), 5,66 t (1H)
(XXVb)	4-ClC_6H_4	Me	4-ClC_6H_4	76	28–30	31,34 30,67	3,09 2,72	1,68 s (3H), 3,05s (3H), 3,63 s (2H), 4,20 m (2H), 5,57 t (1H)
(XVIII)	2,4,6-$Me_3C_6H_2$	Me	Me	93	90–93	34,46 35,00	3,41 3,87	2,50 s (3H), 2,73 s (3H), 3,53 m (2H), 4,70 m(1H)
(XXII)	4-ClC_6H_4	$-(CH_2)_4-$		90	89–92	31,65 32,25	2,42 3,01	2,10 m (4H), 3,63 m (4H), 3,80m (2H), 4,57 m(1H)
(XXVIII)†	4-MeC_6H_4	Me	Me	83				
(XXIX) †	4-MeC_6H_4	Me	4-ClC_6H_4	80				
(XXXa) †	4-MeC_6H_4	Ph	Ph	83				
(XXXb)†	4-ClC_6H_4	Ph	Ph	90				
(XXXIa)‡	4-MeC_6H_4	Ph	Ph	83	45–46	28,21 28,81	3,48 3,54	
(XXXIb)‡	4-ClC_6H_4	Ph	Ph	82	38–39	25,04 25,63	3,42 2,87	

* The aromatic protons are at 7.00-7.80 ppm, the cyclohexene and cyclooctene methylene protons are at 1.60-1.75 ppm, the benzene ring methyl group signals are at 2.38-2.40 ppm (for 4-Me) and 2.30 and 2.60 ppm (for (2,4,6-Me_3).

† The samples are identical to those described in our previous work [5].

‡ The PMR spectra were not taken since salts (XXXIa) and (XXXIb) rapidly decompose in CD_3CN.

Thus, the PMR spectrum of the reaction mixture of (XV) with (VIc) and (VIIa) in CH_2Cl_2 at −50°C shows signals characteristic for the 1,2-adduct: multiplets centered at 5.6 and 4.30 ppm and singlets at 3.50 and 1.65 ppm corresponding to the fragments $\underline{CH}=CH_2$, $\underline{CH_2}=CH$, CH_2SAr, and $Me-\overset{|}{\underset{|}{C}}-C\diagup\diagdown$. These signals already disappear 30 min after warming to 20°C, and the spectrum of the reaction mixture corresponds to the final adducts (XIX) and (XXIIIa), respectively. An analogous rearrangement was previously described for 1,2-chloroarylthio adducts of isoprene [6].

In most cases, we found the formation of the corresponding β-arylthioalkymethyl-4-chlorophenylsulfonium salts (XXIV) and (XXV) for reactions of alkenes with salts (VIII). These salts are rather stable in the case of the derivatives of alkenes (X), (XIII), and (XV). They are characterized by the analytical and spectral data given in Table 3.

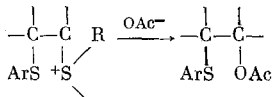
In the case of styrene (XIV) and 1-methylcyclohexene (XI), the corresponding salts (XXVI) and (XXVII) are stable only at low temperature and thus, their structure as β-arylthioalkylmethyl-4-chlorophenylsulfonium salts was confirmed by preparing the corresponding β-acetoxy adducts (XXXV) and (XXXVI) (Table 4).

The formation of an episulfonium salt is clearly demonstrated in the reaction of (VIIIb) with cyclooctene (XIII). The salt obtained (XXIX) was identified by comparison with a known sample relative to melting point, PMR spectrum, and elemental analysis [5]. However, in going to reagents (VIIIc) and (VIIIe), we find the formation of a mixture of salts (A) and (B) in 1:1 ratio according to PMR and elemental analysis. In all these cases, the episulfonium salt is apparently formed initially, but only when the S-aryl group has a sufficiently strong electron-donor substituent does this salt react sufficiently slowly with $4\text{-}ClC_6H_4SMe$ present in the medium to permit its isolation. Analogous behavior is found in the reaction of cyclooctene with (VI). Episulfonium salt (XXVIII) is formed in the case of (VIb), while sulfonium salt (XVII) is formed in the case of (VIc).

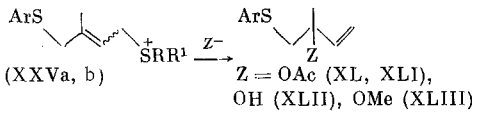
The exclusive formation of episulfonium salts was found in the reactions of (IXb) and (IXc) with cyclooctene and tetramethylethylene. The corresponding salts (XXXa,b) and (XXXIa,b) were obtained in 82-95% yield (see Table 3). Thus, the formation of episulfonium salts using the reagents obtained is possible only when the salts obtained are especially stable [5].

The reactivity of the S-arylepisulfonium salts relative to nucleophiles has been studied in considerable detail [3]. In order to provide further characterization of the S-arylepisulfonium salts obtained in the present work, some of these products (XXXa,b) were reacted with AcO^-. In all cases, the corresponding β-acetoxy adducts (XXXVII) and (XXXVIII) were obtained in invariably high yields (see Table 4).

In order to evaluate the reactivity of type (A) salts, we studied their reactions with the acetate anion and several other nucleophiles. Dialkyl-β-arylthiosulfonium salts (A) obtained using (VI) and (VII) were rather inert towards reaction with AcO^-. Thus, salts (XIX), (XXIIa), and (XVIa) upon treatment with a mixture of glacial acetic acid and sodium acetate for 3 h at 20°C virtually do not yield acetoxy adducts and are obtained unchanged. In their reactivity towards AcO^-, methyl-4-chlorophenyl- and diphenyl-β-arylthiosulfonium salts (A) are similar to the episulfonium salts (B), and the formation of the corresponding acetoxy adducts (XXXII)-(XXXVI), (XL), and (XLI) (see Table 4) proceeds rather readily

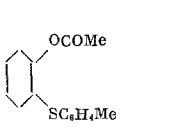
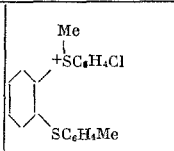
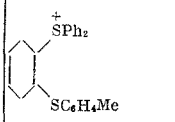
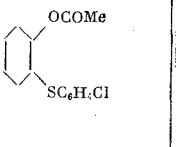
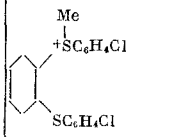
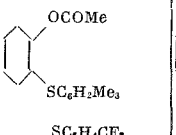
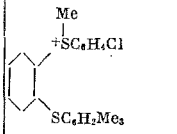
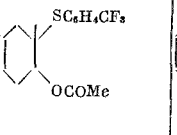
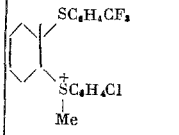
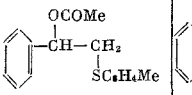
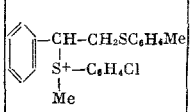
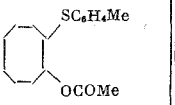
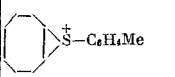
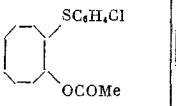
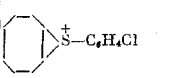
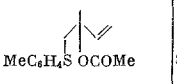
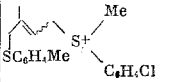
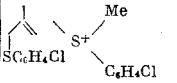


The type (A) salts which are derivatives of isoprene, (XXVa) and (XXVb), react anomalously with AcO^-. The reaction proceeds exclusively by an S_N2' mechanism with the formation of the corresponding β-acetoxysulfides (XL) and (XLI)



These salts react similarly with other nucleophiles. Thus, the treatment of salts (XXIVa) and (XXVa) with saturated aqueous $NaHCO_3$ gives high yields of the corresponding hydroxy adducts (XLII) and (XLIV). Treatment of salt (XXVa) with abs. methanol gives the methoxy adduct (XLIII).

TABLE 4. Characteristics of β-Acetoxy Adducts

Adduct	Formula	Starting compound	Yield, %	Found/Calculated, % C	H	S	PMR spectrum (δ, ppm) CHO	CHS
(XXXII)			53	67,65 / 68,18	6,65 / 5,58	12,02 / 12,12	4,70m	2,98m
			82					
(XXXIII)			73	59,47 / 59,05	5,99 / 5,98	—	4,68m	3,00 m
(XXXIV)			73	69,32 / 69,88	8,44 / 8,22	10,43 / 10,96	4,62m	2,80m
(XXXV)			55	57,47 / 57,83	5,72 / 6,06	—	4,14s	—
(XXXVI)			60	—	—	—	5,76m	3,16m
(XXXVII)*			80					
(XXXVIII)*			78					
(XL)*			55					
(XLI)*			60					

* Identified by GLC and PMR comparison with data in our previous work [7].

The structure of the products of the reaction of type (A) salts with nucleophiles was shown conclusively by their analytical and spectral characterization (see Table 4) and, in the case of (XXXVIII)-(XLI), by comparison with previously prepared samples by GLC and PMR spectroscopy [7].

In previous work, only $RS\overset{+}{S}R^1R^2$ salts, where R, R^1, R^2 are alkyl substituents, were used in Ad_E reactions with alkenes [8]. Only $MeS\overset{+}{S}C_6H_4MeClO_4^-$ and $Me_2\overset{+}{S}SPh_5ClO_4^-$ [9] have been described for salts of type (VI)-(IX). The present method for the preparation of S-arylthiosulfonium salts (VI)-(IX) and the demonstrated feasibility of their use as active transfer agents of the S-aryl group in reactions with alkenes opens a pathway to the preparation of various β-arylthioalkylsulfonium salts which, in turn, may find synthetic use as transfer agents of the β-arylthioalkyl group in nucleophilic substitution reactions.

Wide variation of the substituent in the sulfene chloride and sulfide is possible in this method for preparation of salts (VI)-(IX) and such variation permits control of the stability and reactivity of the type (A) salts

obtained. Preparation of such reagents, for which the major reaction with alkenes would be the formation of type (B) S-arylepisulfonium salts which are more reactive towards nucleophiles, is especially promising.

EXPERIMENTAL

The PMR spectra were taken on Tesla BS-497 spectrometer at 100 MHz in CCl_4, liquid SO_2, and CD_3CN with TMS internal standard. The reaction products were analyzed on a Khrom-4 chromatograph with flame-ionization detector and a 120× 0.3-cm glass column packed with 5% GEXE-60 on Chromaton N-AW-HMDS using helium gas carrier. The reaction products were separated by preparative thin-layer chromatography on an unattached alumina layer with UV indicator using 7:2 hexane–ether eluent.

General Method for the Preparation of Dimethylthioarylsulfonium Salts (VIa-f). A sample of 5 mmoles dimethyl sulfide in 2 ml CH_2Cl_2 was added with stirring to a solution of 5 mmoles sulfene chloride in 3 ml CH_2Cl_2 cooled to −60°C. A white precipitate formed. After 2 min, 5 mmoles $SbCl_5$ in 2 ml CH_2Cl_2 was added and stirred for 5 min, and then 50 ml cooled abs. ether was added. The temperature was raised to ~20°C. The precipitate was removed by filtration and washed on the filter with two 30-ml pentane portions and dried for 30 min at 1-2 torr. The yields and properties are given in Table 1.

General Method for the Preparation of Tetramethylenethioarylsulfonium Salts (VIIa) and (VIIb). These salts were prepared analogously to the above procedure. The analytical data and PMR spectra are given in Table 1.

General Method for the Preparation of 4-Chlorophenylmethylthioarylsulfonium Salts for Taking the PMR Spectra of (VIIa-f). A solution of 1 mmole sulfene chloride in 1 ml liquid SO_2 and 1 mmole SbF_5 in 1 ml liquid SO_2 was added with stirring to a suspension of 1 mmole 4-chlorophenylmethylsulfide in 2 ml liquid SO_2 cooled to −50°C. The stirring was continued at this temperature for an additional 5 min and the PMR spectra taken are presented in Table 2.

General Method for the Preparation of Diphenylthioarylsulfonium Salts (IXa-d). A sample of 1 mmole diphenyl sulfide in 1 ml CH_2Cl_2, 1 mmole sulfene chloride and 1 mmole $SbCl_5$ in 1 ml CH_2Cl_2 was mixed at −60°C. The salts prepared were characterized according to their ^{13}C NMR spectra and the products of their reaction with alkenes.

Preparation of Sulfonium Salts (XXIVa,b,c) and (XXVa,b) from (VIIIb,c,d) and Alkenes (X) and (XV). A sample of 2 mmole sulfene chloride and 2 mmole $SbCl_5$ in 1 ml CH_2Cl_2 was added with stirring to a suspension of 2 mmole 4-ClC_6H_4SMe in 2 ml CH_2Cl_2 cooled to −50°C. After 2 min, a solution of 3 mmole alkene in 1 ml CH_2Cl_2 was added. After an additional 5 min, the reaction mixture was poured into abs. ether cooled to −60°C with rapid stirring. An abundant precipitate formed. The ether was decanted and the precipitate was washed with cold ether and 1:1 ether–pentane and two 50-ml pentane portions. The precipitate was then separated by filtration and dried for 30 min at 1-2 torr. The analytical and spectral data for the salts obtained are given in Table 3.

Preparation of Sulfonium Salts (XVIa,b), (XVII), (XVIII), (XIX) from (VIb,c,d) and Alkenes (X), (XIII), (XIV), and (XV). A sample of 1.5 mmole alkene in 1 ml CH_2Cl_2 was added to a suspension of 1 mmole reagent in 2 ml CH_2Cl_2 at −50°C. The reagent completely dissolved upon warming to −30 to −10°C. After 5 min, the reaction mixture was poured into 100 ml abs. ether cooled to −60°C with rapid stirring. The salt precipitate formed was treated as described above. The analytical and spectra data are given in Table 3.

Preparation of Sulfonium Salts (XXa,b) (XXI), (XXIIIa,b) from Reagents (VIIa,b) and Alkenes (X), (XIII), (XIV), and (XV). A sample of 1.5 mmole alkene in 1 ml CH_2Cl_2 was added to a solution of 1 mmole reagent in 2 ml $MeNO_2$ at −20°C. The temperature was raised to −10 to 0°C, maintained for 5 min, and then, the mixture was poured into abs. ether cooled to −60°C with rapid stirring. The separation of the precipitate was carried out as described above. The analytical and spectra data of the salts obtained are given in Table 3.

Preparation of S-Arylepisulfonium Salts (XXVIII), (XXIX), and (XXXa,b) from (VIIIb), (VIb), (IXb), and Cyclooctene. A sample of 1.5 mmole cyclooctene in 1 ml CH_2Cl_2 was added to a solution of 1 mmole reagent in 2 ml CH_2Cl_2 (2 ml $MeNO_2$ in the case of (VIb)) at −20°C. The salts were separated by the usual procedure. The episulfonium salts obtained were identical in their analytical data and PMR spectra to those previously prepared [5].

In the case of reagents (VIIIc) and (VIIIe), the product obtained was 1:1 mixture of episulfonium and sulfonium salts; the product ratio was found by elemental analysis and PMR spectroscopy.

Preparation of S-Arylepisulfonium Salts (XXXIa,b) from Tetramethylethylene and (IXb,c). The corresponding sulfene chloride (1 mmole) and 1 mmole $SbCl_5$ in 1 ml CH_2Cl_2 were added to a solution of 1 mmole diphenyl sulfide in 3 ml CH_2Cl_2 at −60°C to yield a green solution of the reagent. After 5 min, 1.5 mmole tetramethylethylene in 1 ml CH_2Cl_2 was added and the mixture was kept for 10 min at −60°C. Then, the mixture was poured with rapid stirring into 100 ml cooled abs. ether. An abundant white precipitate formed, which was separated by the usual procedure. The analytical data for the salts prepared are given in Table 3.

General Method for the Preparation of Acetoxy Adducts (XXXII)-(XXXVI), (XL), and (XLI) from Salts (XXIV)-(XXVII). A solution of 3 mmoles sulfene chloride in 1 ml CH_2Cl_2 was added with stirring to a solution of 3 mmoles methyl 4-chlorophenyl sulfide (or diphenyl sulfide) in 5 ml CH_2Cl_2 cooled to −60°C. Then, a solution of 3 mmoles $SbCl_5$ in 1 ml CH_2Cl_2 was added. After 1 min, 3.5 mmole olefin in 2 ml CH_2Cl_2 was added to the solution of the salt obtained (VIII) or (IX) and after an additional 5 min, a mixture of 2.4 g anhydrous sodium acetate and 24 ml glacial acetic acid was added. The mixture was stirred for 30 min at −60°C and then for 40 min at 20°C, neutralized with saturated aqueous sodium bicarbonate, and extracted with chloroform. The chloroform extracts were dried with anhydrous sodium sulfate. After removal of chloroform, the product was purified by means of thin-layer chromatography (see Table 4).

Preparation of Hydroxy Adducts (XLII) and (XLIV) from Salts (XXIVa) and (XXVa). A saturated aqueous solution of sodium bicarbonate (10 ml) was added to a suspension of 2 mmoles salt in 5 ml CH_2Cl_2 at 0°C and then stirred for 2 h at 20°C. The product was extracted with two 50-ml portions of chloroform. The chloroform extracts were washed with water and dried with anhydrous sodium sulfate. The solvent was distilled off in vacuum and the product was separated by thin-layer chromatography.

(XLII): 0.33 g (75%), identified by comparison with the analogous adduct obtained in our previous work [3]. PMR spectrum (δ, ppm): 2.60 m (CHS), 3.50 m (CHO), 2.50 s (OH).

(XLIV): 0.33 g (80%). Found: C, 69.58; H, 7.97; S, 14.64%. Calculated for $C_{12}H_{16}OS$: C, 69.23; H, 7.69; S, 15.33%. PMR spectrum (δ, ppm): 1.28 s (3H, MeC), 2.30 s (3H, MeAr), 2.44 m (1H, OH), 3.02 m (2H, CH_2S), 5.10 m (2H, $CH_2=$), 5.82 m (1H, CH=), 7.10 m (4H, Ar).

Preparation of Methoxy Adduct (XLIII) from Salt (XXVa). A sample of 10 ml abs. methanol was added to a suspension of 3 mmoles salt in 5 ml CH_2Cl_2 at 0°C. The mixture was stirred for 2 h at 20°C and separated by the procedure described above to yield 0.47 g (72%) (XLIII). PMR spectrum (δ, ppm): 1.32 s (3H, MeC), 2.28 s (3H, MeAr), 2.97 s (2H, CH_2S), 3.08 s (3H, OMe), 5.24 m (2H, $CH_2=$), 5.80 m (1H, CH=), 7.07 m (4H, Ar).

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CONCLUSIONS

A general method was developed for the preparation of arylthiosulfonium salts which are active transfer agents for the S-aryl group in reactions with alkenes, leading to the formation of β-arylthioalkylsulfonium or S-arylepisulfonium salts.

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