ARYL(BISARYLTHIO)SULFONIUM SALTS AS TRANSFER AGENTS FOR THE S-ARYL GROUP IN THE PREPARATION OF S-ARYLEPISULFONIUM SALTS AND CHARACTERISTICS OF STABLE S-ARYLEPISULFONIUM SALTS

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The simplest method for the preparation of episulfonium (ES) salts is the reaction of alkenes with SR^+Y cationoids (where Y is a nonnucleophilic anion) which are generated in situ in systems $RSCl+AgBF_4$ [1] or $RSCl+SbCl_5$ [2]. However, the alkylsulfonium and arylsulfonium cations are unstable even in solution [3] and thus, the need arises for finding stabilized reagents of the general type $[RS \cdot Stab]^+Y^-$ capable of serving as active transfer agents for the RS^+ group. For R = Me, this problem has been solved with the use of dimethyl sulfide as the stabilizer; the reagent $MeS^+(SMe)_2SbCl_6^-$ (I) is rather stable and convenient for the preparation of S-methyl-ES salts [4].

The aim of the present work was clarification of the feasibility of preparing analogous reagents for the more general case when R = Ar.

We have found that $ArS^+(SAr)_2Y^-$ complexes (II) are readily obtained in solution [5] by reactions analogous to those described for the synthesis of (I) [4]

$$3(ArS)_2 + 3SbCl_5 \rightarrow 2[ArS\overset{+}{S}(Ar)\,SArSbCl_6^-] + SbCl_3 \text{ (method A)}$$

$$ArSCl + (SAr)_2 + SbCl_5 \rightarrow ArS\overset{+}{S}(Ar)SArSbCl_6^- \text{ (method B)}$$

or SbF_5 (II a—d), or SbF_5Cl^-

Ar = Ph (a), 4-ClC_6H_4(b), 4-MeC_6H_4(c), 2,4,6-$Me_3C_6H_2$ (d).

Virtually all the formation of salts (IIa-d) occurs immediately upon mixing of stoichiometric quantities of the reagents at −50 to −70°C in methylene chloride or liquid SO_2.* The solutions of salts (IIa-e) obtained remain without change for several hours at −50 to −20°C. Salts (II) may be isolated in the free state upon the removal of SO_2 in vacuum at −20°C or crystallization from 1-1.5 M solutions in CH_2Cl_2 at −75°C. However, at 20°C, they retain activity for only several minutes. Insufficient stability and hygroscopicity did not permit characterization of the salts by elemental analysis.

^{13}C NMR spectra of the reaction mixtures obtained by method A or B served to evaluate the formation of salts (IIa-d). These spectra recorded at −50 to −70°C did not show signals of the starting reagents but displayed two sets of aromatic ring ^{13}C signals in 2:1 intensity ratio. This corresponds to linear structure (II) containing two equivalent S-aryl residues attached to a central S-arylsulfonium group. Upon warming to ~−30°C, averaging of the two subspectra occurs which, apparently, results from rapid intra- and/or intermolecular exchange of S-aryl groups. A similar exchange was found in mixtures containing type (I) salts [6].†

The formation of type (II) intermediates was postulated as a possible step in the disproportionation of asymmetrical disulfide in acid medium [7] but these complexes have not been described as actual species.

*Data concerning the completeness of the reaction were obtained by studying the low-temperature ^{13}C NMR spectra; the reagent yield was also estimated relative to the yield of ES salts obtained from them (see below).
†The spectral data which indicate a greater likelihood for a linear structure for (IIa-d) than the previously proposed cyclic structure [5] will be given in a separate communication.

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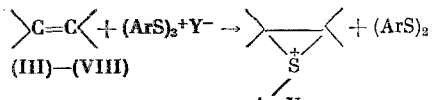
The capacity of salts (IIa-d) to serve as transfer agents for the ArS^+ group was checked in reactions with the following alkenes: cis-cyclooctene (III), norbornene (IV), tetramethylethylene (V), cyclohexene (VI), 1-methylcyclohexene (VII), and styrene (VIII). These Ad_E reactions proceed very rapidly even at −60°C with the formation of the corresponding S-arylepisulfonium (S-aryl-ES) salts according to the scheme



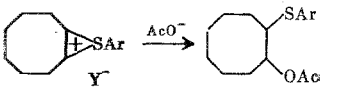
(III)—(VIII)

Ar Y⁻
S-aryl-ES
(IX a—d), (XI b—f); (XII a, b); (XIX)

The reaction with (III) was studied in greatest detail. In this case, we were able to isolate cyclooctene-S-arylepisulfonium hexachloroantimonates* (IXa-d) in approximately 100% yields.

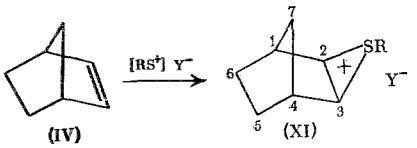
Salts (IXa-d) are weakly hygroscopic and are completely characterized by the analytical and spectral data given in Table 1. Their PMR spectra show a 2H multiplet for the methine protons of the episulfonium ring in the vicinity of 4.7 ppm [8]. The low solubility of the hexachloroantimonates in most solvents did not permit study of their ^{13}C NMR spectra but this study was carried out for cyclooctene-S-mesitylepisulfonium tetrafluoroborate (IXe) obtained according to our previous work [1]. The ^{13}C NMR spectrum of (IXe) shows only four signals for the cyclooctane ring due to a plane of molecular symmetry at 26.1, 26.2, 28.2, and 77.0 ppm. The downfield signal corresponds to the methine ^{13}C atom of the episulfonium ring.

In accord with the pattern for opening of ES derivatives of cyclooctene [8], the reaction of (IXa-e) with acetate anion yields 2-acetoxycyclooctyl aryl sulfides (Xa-d) (see Table 1)



(IXa-e) (Xa-d)

The reactions of salts (IIb-d) with (IV) gave good yields of the corresponding norbornene-S-arylepisulfonium salts (XIb-d). The salts are also quite stable in the solid state and only slightly hygroscopic though their low solubility and insufficient stability in solution hinders their spectral investigation.† Thus, the analogous salts (XIe) and (XIf) with the more stable SbF_6^- counter-ion were obtained according to our previous procedure [1] as well as norbornene-S-methyl-ES (XIIa) and (XIIb)



(IV) (XI)

Y = $SbCl_6$, R = 4-ClC_6H_4 (XIb), 4-MeC_6H_4 (XIc), 2,4,6-$Me_3C_6H_2$ (XId); Y = SbF_6, R = 4-ClC_6H_4 (XIe), 2,4,6-$Me_3C_6H_2$ (XIf); R = Me, Y = $SbCl_6$ (XIIa), SbF_6 (XIIb).

The analytical and spectral data for ES salts (XI) and (XII) are given in Table 2. The PMR spectra of (XIb,c,e,f) and (XIIa,b) have the following characteristic signals: broad singlets for the episulfonium ring methine protons at 4.3-5.1 ppm and 2H singlets for the 1- and 4-protons of the norbornene system at 3.2-3.5 ppm. The ^{13}C NMR spectrum of (XIIb) (δ, ppm, from CH_2Cl_2 recalculated for TMS) showed peaks at 63.1 (C-2 and C-3), 38.8 (C-1 and C-4), 30.7 (Me), 25.2 (C-5 and C-6) and 18.5 (C-7). The spectrum corresponds to structure (XIIb) and the similarity of the PMR spectra of all the norbornene salt derivatives permits their assignment to the same structural type.

Salts (XI) and (XII) are the first reported stable bridged ions in the norbornene series in the free state. Previously, this type of structure was found only for the mercurium ion observed by PMR spectroscopy in superacid media [9].

*Olefin (III) was also reacted with $[(4\text{-}ClC_6H_4S)_3]^+SbF_5Cl^-$ and the corresponding ES salt was obtained in 98% yield. This product was identified on the basis of PMR spectroscopy and the acetoxy adduct obtained (Xb) in 90% yield.

†For example, salt (XId) in liquid SO_2 at −70°C is quantitatively converted in only 1 h to chloro adduct (XIV) (R = 2,4,6-$Me_3(C_6H_2)$); salts (XIc) and (XId) in $(CD_3)_2CO$ remain for only 10-15 min at −95°C while (XIb) reacts with this solvent even at −95°C.

TABLE 1. Characteristics of Cyclooctene-S-aryl-ES salts (IXa-e) and 2-Acetoxy-1-arylthiocyclooctanes (Xa-d)

Salt	Yield, %	Mp, °C, Bp, °C (mm Hg)*	Found/Calculated, %				PMR spectrum (characteristic signals) (δ, ppm)†		
			C	H	S	Cl	HCS+(2H)	CH(2H) ‡	
(IXa)	85	99–100	30,73 / 30,36	3,42 / 3,46	5,67 / 5,79	38,97 / 38,40	4,79 m	2,86 m	
(IXb)	95	97–99	28,25 / 28,58	2,89 / 3,08	5,54 / 5,45	43,04 / 42,19	4,71	2,79	
(IXc)	96	108–110	31,76 / 31,45	4,10 / 3,70	5,88 / 5,60	38,00 / 37,13	4,69 m	2,84 m	
(IXd)	89	115–116	33,60 / 34,26	4,10 / 4,23	5,34 / 5,38	35,40 / 35,70	4,70 m	2,92 m	
(IXe,) **	41	102–103	58,30 / 58,63	7,04 / 7,24	8,95 / 9,21		4,67 m	2,95 m	
(Xa)	97	140(2)	69,44 / 69,04	7,94 / 7,96	11,64 / 11,50		CHS(1H) 3,39 d.t	CHOAc(1H) 4,92 d.t	OAc(3H) 1,77 s
(Xb)	88	150(2)	61,29 / 61,43	6,78 / 6,77	10,22 / 10,25	11,31 / 11,33	3,26 d.t	4,88 d.t	1,77 s
(Xc)	99	160(3)	70,34 / 69,82	8,33 / 8,27	10,44 / 10,96		3,22 d.t	4,84 d.t	1,78 s
(Xd)	95	170(2)	71,17 / 71,25	8,94 / 8,75	10,03 / 10,00		3,10 d.t	4,87 d.t	1,64 s

* The bath temperature during distillation is given.

† The spectra were recorded relative to TMS internal standard for 10–15% solutions in CD_3CN at −40°C for ES salts (IXa-d) and in CCl_4 at 30°C for adducts (Xa-d). The spectra for all these compounds also have aromatic proton signals and cyclooctane ring proton signals at 1.3-2.0 ppm; the 1,2 arrangement of substituents in (Xa-d) was confirmed by H−H double resonance data.

‡ The 2H multiplet is not related to the α-carbon proton signals (α relative to the ES bridge) and is presumably related to the trans-annular protons at the γ-carbons.

** The counterion is BF_4^- in this case.

TABLE 2. Characteristics of Norbornene ES Salt Derivatives (XIb-f) and (XIIa,b)

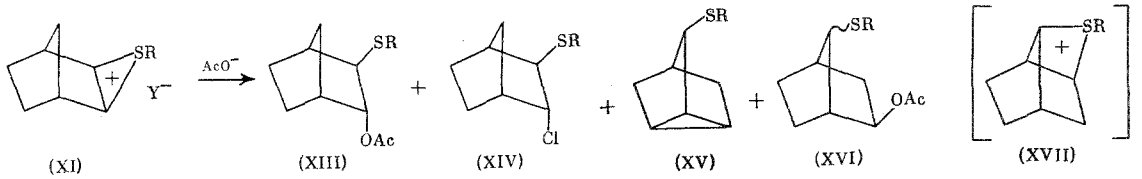
Salt	Yield, %	Mp (dec.) °C	Found/Calculated, %				PMR spectrum (characteristic signals) (δ, ppm)*	
			C	H	S	Cl	$HC^{2,3}$	$HC^{1,4}$
(XIb)	98	72–74	26,90 / 27,29	2,60 / 2,47	5,89 / 5,60	45,80 / 43,37	Not obtained	
(XIc)	93	68–69	30,00 / 30,47	3,00 / 3,11			4,68 s 5,21 s	3,42 s (a) 3,39 s (b)
(XId)	98	75–76	32,50 / 33,14	3,70 / 3,65	5,74 / 5,55	38,10 / 36,68	4,59 s 5,13 s	3,50 s (a) 3,49 s (b)
(XIe)	Without separation						4,56 s	3,30 s (c)
(XIf)	Same						4,55 s	3,49 s (c)
(XIIa)	94	87–88	19,20 / 20,17	2,90 / 2,73	7,50 / 6,72	44,60 / 44,75	4,66 s	3,19 s (b)
(XIIb)	49	170–172	26,26 / 25,46	3,85 / 3,45	8,93 / 8,43		4,58 d, J=1 4,29 d, J=1	3,60 s (d) 3,19 s (e)

* The PMR spectra were taken relative to TMS internal standard: a) in liquid SO_2 at −75°C, b) in $(CD_3)_2CO$ at −95°C, c) in 4:1 SO_2–$CDCl_3$ at −70°C, d) in CH_2Cl_2 at 36°C, and e) in CD_3CN at 36°C. The spectra of the ES salts (with the exception of (XIIa,b)) also have aromatic proton signals.

TABLE 3. Ratio of Products (XIII)-(XVI) in the Reactions of ES Salts (XIb-f) with Acetate Anion

Starting salt	Overall yield, %	Adduct ratio			
		(XIII)	(XIV)	(XV)	(XVI)
(XIb) (R=4-ClC_6H_4; Y=$SbCl_6$)	80	4	2	2	1
(XIc) (R=4-MeC_6H_4; Y=$SbCl_6$)	97	4	2	0,5	–
(XId) (R=2,4,6-$Me_3C_6H_2$; Y=$SbCl_6$)	97	20	1	1	–
(XIe) (R=4-ClC_6H_4; Y=SbF_6)	82	–	–	3	1
(XIf) (R=2,4,6-$Me_3C_6H_2$; Y=SbF_6)	90	3	–	1	–

The nature of the adducts formed by treating salts (XI) and (XII) with acetate anion under standard conditions for ES salt reactions [1] depends on the nature of the aryl substituent, counterion, and reaction conditions (Table 3).



The structures of (XIII)-(XVI) were confirmed using PMR spectroscopy (Table 4) by comparison with known samples [10]. The appearance of chloro adducts (XIV) in the acetolysis products apparently results from the instability of the salts (XIb-d) in solution (see above). The formation of the acetoxy adduct (XIII) corresponds to the usual direction for the opening of ES salts by the action of nucleophiles and this is naturally the major pathway for the most stable salt (XId) which contains a strong electron-donor substituent at the sulfur atom. In going to salt (XIb) which has an electron-withdrawing 4-ClC_6H_4S group, the fraction of Wagner–Meerwein rearrangement products (XVI) and tricyclene products (XV) increases. Zefirov et al. [10] have reported that precisely this type of products is formed when running the reaction of norbornene with ArSCl under conditions favorable for the formation of episulfonium ion intermediates. In the case of salts (XIe) and (XIf), the fraction of unrearranged product (XIII) in the mixture is significantly reduced, which corresponds to the known facilitation of rearrangement upon going to a less nucleophilic counterion [11].

TABLE 4. Characteristics of Norbornene Adducts (XIII)-(XVII)*

Adduct	Found/Calculated, %				PMR spectrum (δ, ppm)†			
	C	H	S	Cl	HCS	HCZ	OAc	HC¹,⁴
(XIIIb)	60,37 / 60,71	5,66 / 5,73	10,92 / 10,79	11,82 / 11,97	2,86 t	4,74 t	1,97 s	2,58 s 2,18 s
(XIVb)	Identical to that described in [10]				2,96 t	3,98 t	–	2,44 s 2,22 s
(XVb)	66,25 / 65,95	5,57 / 5,53			3,06 s	–	–	1,81 s 1,96 s
(XIIIc)	69,03 / 69,57	7,31 / 7,25	11,72 / 11,59		2,86 t	4,71 t	1,92 s	2,57 s 2,19 s
(XIVc)	66,49 / 66,53	6,54 / 6,73	13,22 / 12,67	14,66 / 14,06	2,96 t	3,96 t	–	2,44 s 2,28 s
(XIIId)	71,01 / 71,18	7,91 / 7,95	10,39 / 10,53		2,58 t	4,58 t	1,82 s	1,88 s (in region 2,4–2,5)
(XIVd)	68,85 / 68,45	7,68 / 7,49	11,36 / 11,41	12,56 / 12,66	2,68 t	3,82 t	–	
(XVd)‡					2,80 s	–	–	1,78 s 2,06 s
(XVIb) (two isomers)	61,06 / 60,71	5,73 / 5,73			3,37 s 3,02 s	4,54 q, J=3 4,47 q, J=3	1,85 s 1,95 s	2,22 s (2H) 2,34 s (2H)
(XVIII)	60,23 / 59,96	8,05 / 8,05	16,62 / 16,01		2,29 s	4,65 t	1,95 s	2,50 s 2,12 s

* Product yields given in Table 3.

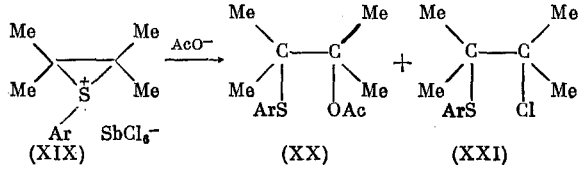
† The PMR spectra were recorded in 15-20% solutions in CCl_4 relative to TMS internal standard. The spectra of all the products except (XVIII) also have aromatic proton signals. For (XIII), (XIV), and (XVIII), the 1,2-arrangement of the Z and SR groups was confirmed in a H–H double resonance experiment.

‡ The product could not be completely purified; its structure was confirmed by mass spectroscopy.

The formation of products (XV) and (XVI) indicates that salts (XI) are capable of rearrangement in solution with the formation of thietanium salts (XVII). However, this rearrangement could not be observed by PMR spectroscopy by maintenance of solutions of (XIe) and (XIf). Thus, the spectrum of a solution of (XIe) in liquid SO_2 at 0°C after 30 min shows the complete absence of signals of the starting salt and new signals do not appear. Apparently, the formation of (XVII) is sterically unfavorable in light of the difficulty of forming thietanium salts [12] and under conditions initiating the rearrangement in the absence of a nucleophile, salt (XI) is decomposed.

In the cases of S-methyl salts (XII), reaction with AcO^- leads exclusively to the formation of the unrearranged product, 2-acetoxy-3-methylthionorbornane (XVIII), in 95% yield and PMR spectroscopy indicated that salt (XIIb) does not have any tendency to undergo transformation, even after 2-3 h at 35°C in CH_2Cl_2.

The reaction of (IId) with (V) also gave the corresponding ES salt (XIX) as a stable product in 84% yield. This salt was identified by elemental analysis and reaction with acetate anion leading to the formation of 2,3-dimethyl-2-acetoxy-3-mesitylthiobutane (XX) (63%) and 2,3-dimethyl-2-chloro-3-mesitylthiobutane (XXI) (35%)



(XIX) (XX) (XXI)

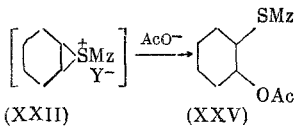
In the reactions of (VI)-(VIII) with (IIc,d), we were unable to isolate ES salts (XXII)-(XXIV) in the free state; upon removal of solvent, these salts decompose even at −20°C. Thus, the formation of ES salts in these cases was established using the results of the reaction of the alkene–(II) complex with a nucleophile (acetate

TABLE 5. Analytical and Spectral Data for Acetoxy Adducts (XXV)-(XXVII)

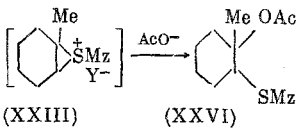
Compound	Yield, %	Found/Calculated, %			PMR spectrum (characteristic signals) (δ, ppm)*		
		C	H	S	CHS	CHOAc	OAc
(XXV)	81	69,95 / 69,86	8,61 / 8,22	10,69 / 10,96	2,78	4,65	1,76
(XXVI)	56	73,44 / 72,61	7,50 / 7,01	9,11 / 10,19	3,50	–	1,66
(XXVII)	60	70,90 / 70,59	8,75 / 8,50	10,33 / 10,46	2,90	5,62	1,92

*The spectra were recorded in CCl_4 at 30°C relative to TMS internal standard. The spectra of all these compounds also have aromatic proton signals. Products (XXV) and (XXVI) have cyclohexane ring proton signals while (XXVII) has benzene ring signals.

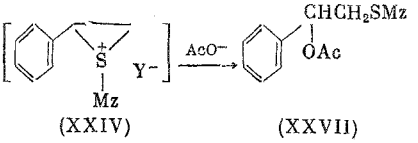
anion). This "quenching" reaction proceeds as readily as for known ES salts and gives good yields of the corresponding β-acetoxythioethers identified by spectral and analytical data (Table 5).



(XXII) (XXV)



(XXIII) (XXVI)



(XXIV) (XXVII)

Y = $SbCl_6^-$; Mz = 2,4,6-$Me_3C_6H_2$.

These results show that the new reagents $(ArS)_3^+Y^-$ are indeed active transfer agents for ArS^+ groups in electrophilic reactions with alkenes. The use of these reagents permits not only more facile production of ES salts but also the isolation of these salts in the free state when they are sufficiently stable.

EXPERIMENTAL

The gas–liquid chromatographic analysis was carried out on an LKhM-8-MD chromatograph in 1-2 m × 4 mm columns packed with 3-5% OV-101 and XE-60. The mass spectra were taken on a Varian CH-6 mass spectrometer and the PMR spectra were taken on a TeslaBS-496 spectrometer at 100 MHz. The ^{13}C NMR spectra were taken on a Bruker WP-60 spectrometer at 15.08 MHz. The reaction products were preparatively separated on 24 × 30-cm glass plates coated with a 2-mm-thick unattached silica layer. The purification and drying of the solvents were carried out by standard methods. All the operations for the preparation and transformation of salts (II) and the ES salts were carried out in a stream of dry argon.

General Method for the Preparation of Aryl(bisarylthio)sulfonium Salts (IIa-d). 1) Reaction of diaryl disulfides with $SbCl_5$. A solution of 3.0 mmoles $SbCl_5$ in 2-3 ml CH_2Cl_2 was added with efficient stirring and cooling to a solution of 3.0 mmoles diaryl disulfide in 15-20 ml CH_2Cl_2 at −70°C. The reaction mass became highly colored and then lightened after 1-2 min. The reaction gave 2.0 mmoles salt (II).

2) Reaction of $ArSCl + (ArS)_2 + SbX_5$ (X = Cl or F). A sample of 3.0 mmoles SbX_5 in 1-2 ml solvent was added to a solution or suspension of 3.0 mmoles ArSCl and 3.0 mmoles $(ArS)_2$ in 5 ml solvent (CH_2Cl_2 for X = Cl, and liquid SO_2 for X = F). The solution obtained contains 3.0 mmoles salt (II). Crystallization from CH_2Cl_2 (or the evaporation of SO_2) at −75 to −80°C permitted the isolation of salt (II) in its free state. These salts may be stored without change for at least 12 h at −78°C.

Stable ES Salts (IXa-d) and (XIb-e). These salts were prepared by a standard method. A solution of 2 mmoles (III) or (IV) in 2-3 ml CH_2Cl_2 was added at −75°C to a freshly prepared solution of 2 mmoles salt (II) in 20 ml CH_2Cl_2. The mixture was stirred for an additional few minutes at this temperature and then poured into 200 ml abs. ether cooled to −70°C. The ES salt precipitate was filtered in an argon stream on a dry-ice-cooled filter, washed with two 100-ml ether portions to remove $(ArS)_2$, and dried in vacuum at 20°C. The physical characteristics of these salts are given in Tables 1 and 2.

Tetramethylethylene-S-mesitylepisulfonium Hexachloroantimonate (XIX). A sample of (XIX) was prepared analogously to the above procedure in 84% yield. Found: C, 29.26; H, 3.71; S, 5.73; Cl, 38.04%. Calculated for $C_{15}H_{23}SSbCl_6$: C, 31.62; H, 4.07; S, 5.62; Cl, 37.33%. The lifetime of (XIX) at 20°C was limited to 15-30 min but it may be stored without noticeable change at −78°C for 24 h.

Cyclooctene-S-mesitylepisulfonium Tetrafluoroborate (IXe). A sample of 2.5 mmoles Br_2 was added to a solution of 2.5 mmoles $(2,4,6\text{-}Me_3C_6H_2S)_2$ in 15 ml CH_2Cl_2 at −30°C and the mixture was stirred for 10 min at −30 to 0°C. Then, a solution of 5.2 mmoles $AgBF_4$ in 3 ml CH_2Cl_2 was added at −50°C to 5 mmoles $2,4,6\text{-}Me_3C_6H_2SBr$ formed and the mixture was stirred for 10 min. Then, 5 mmoles cyclooctene (III) was introduced and the mixture was maintained for 10 min at −25 ± 5°C. The solution of the ES salt was separated from the AgBr precipitate by decantation and filtration with cooling. The filtrate was evaporated at −20°C (1 torr) to 5-7 ml and then poured into 50-70 ml abs. ether cooled to −50°C. The (IXe) salt precipitate was filtered with cooling and dried in vacuum. The characteristics of this product are given in Table 1.

Norbornene-S-methylepisulfonium Hexafluoroantimonate (XIIb). Salt (XIIb) was obtained from 2.5 mmoles $(MeS)_2$, 2.5 mmoles Br_2, 5 mmoles norbornene (IV), and 5.1 mmoles $AgSbF_6$ by an analogous procedure (see Table 2).

Norbornene-S-methylepisulfonium hexachloroantimonate (XIIa) was obtained by the reaction of (IV) with $MeS_3^+SbCl_6^-$ by analogy to the procedure of Capozzi et al. [4]. The characteristics of this product are given in Table 2.

Solutions of cyclohexene-, 1-methylcyclohexene-, and styrene-S-arylepisulfonium hexachloroantimonates (XXII), (XXIII), and (XXIV), respectively, were obtained by the reaction of equimolar quantities of the alkenes and reagent (IId) in CH_2Cl_2 at −60°C.

Acetoxy Adducts of ES Salts. These adducts were prepared by a standard method by treating a solution or suspension of the ES salt in CH_2Cl_2 with an excess (usually 10-20%) of a mixture of sodium acetate (or Me_4NOAc) in acetic acid at −20 to +20°C. Subsequent work-up entailed ether extraction, washing with water, aq. $NaHCO_3$, and water, and removal of the solvent. Thin-layer chromatography on silica gel, usually with 5:1 hexane–ether eluent, was used to purify the acetoxy products obtained and/or to effect separation of the products obtained. The characteristics of the products obtained are given in Tables 1, 4, and 5.

2,3-Dimethyl-2-acetoxy-3-(2,4,6-trimethylphenylthio)butane (XX). Treatment of ES salt (XIX) by acetate anion for 30 min at −75°C in CH_2Cl_2 yielded (XX). Separation was analogous to the above procedure to yield 63% (XX) with bp 130°C (2 mm). Found: C, 69.37; H, 8.90; S, 10.85%. Calculated for $C_{17}H_{26}O_2S$: C, 69.58; H, 8.93; S, 10.93%. PMR spectrum (CCl_4, δ, ppm, relative to TMS): 1.11 s (6H, Me_2C), 1.73 s (6H, Me_2COAc), 1.96 s (3H, OAc) and aromatic ring proton signals. In addition to (XX), 2,3-dimethyl-2-chloro-3-(2,4,6-trimethylphenylthio)butane (XXI) was isolated in 35% yield and identified by comparison with a known sample.

CONCLUSIONS

1. Aryl(bisarylthio)sulfonium salts which are new electrophilic reagents were obtained and characterized by ^{13}C NMR spectroscopy.

2. The feasibility of using these reagents in Ad_E reactions with alkenes was shown.

3. S-Arylepisulfonium salt derivatives of cyclooctene, norbornene, and tetramethylethylene were isolated as pure compounds for the first time.

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AZACYCLOALKENYLATION OF THIOPHENES AND N-METHYLPYRROLE WITH 4-PIPERIDONES IN SULFURIC ACID

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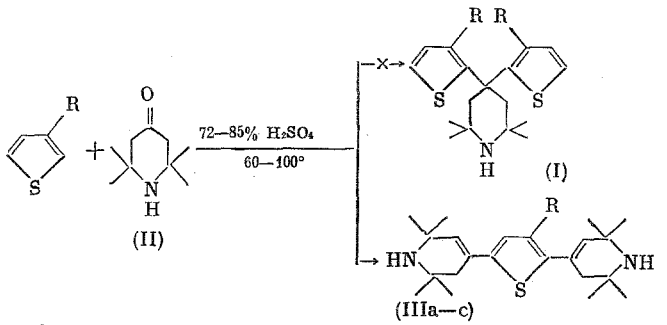
When investigating biological membranes with spin probes, paramagnetic derivatives of the oxazolidine series are widely used [1, 2], which, however, are available with difficulty [3] and are not versatile due to their ready hydrolysis. Similarly constructed derivatives of the 2,2,6,6-tetramethylpiperidine series with a different position of the paramagnetic center seem promising in this respect.

2,2,6,6-Tetramethyl-4,4-di(2-thienyl)piperidine (I) might serve as a starting material for the synthesis of such derivatives. The thiophene ring of (I) is potentially suitable for creating aliphatic functionalized units [4]. Attempts to obtain this compound were undertaken by us by condensing two equivalents of thiophene with one equivalent of triacetonamine (II) in 72% H_2SO_4. As is known [5], thiophene condenses under analogous conditions with ketones, including cyclic ketones, with the formation of di(2-thienyl)alkanes.

However, in place of the expected (I), the product isolated was the condensation product of two equivalents of (II) with one equivalent of thiopene, viz. 2,5-bis(2,2,6,6-tetramethyl-1,2,5,6-tetrahydropyrid-4-yl)thiophene (IIIa), in 65-70% yield, which was not appreciably changed at a stoichiometric ratio of reagents. Similarly, 3-bromo- and 3-methylthiophenes reacted giving bisazacycloalkenylthiophenes (IIIb) and (IIIc) (Table 1). Compound (IIIb) was formed more readily, but (IIIc) with more difficulty than (IIIa). To achieve a good yield in the latter case it was necessary to increase the acid concentration and reaction temperature.



R = H (a), Me (b), Br (c).

The structures of products (III) were confirmed by analytical and spectral data and by chemical conversions.

Mass spectra of (IIIa-c) (Table 2) corresponded to the presence of a 2,2,6,6-tetramethyl-1,2,5,6-tetrahydropyridine ring [6]. The most intense peak in the spectra corresponded to the $(M^+ - Me)$ ion. The molecular ion peak had a significant intensity (~17%) as did the peak for the doubly charged ion $(M - Me)^{2+}/2$. Ions also observed were $(M^+ - 2Me)$, $(M^+ - Me, - HN{=}CMe_2)$ and $(M^+ - H, - 2Me, - HN{=}CMe_2)$. Another direction of fragmentation was apparently linked with fission of the bond between the thiophene and one of the tetrahydropyridine rings, which corresponds to a peak of m/z 122 ($C_9H_{16}N^+ - Me$) present in the spectra of all these compounds.

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