

ARYL-BIS(THIOARYL)SULFONIUM SALTS AND THEIR USE FOR THE PREPARATION
OF S-ARYL-EPISULFONIUM SALTS

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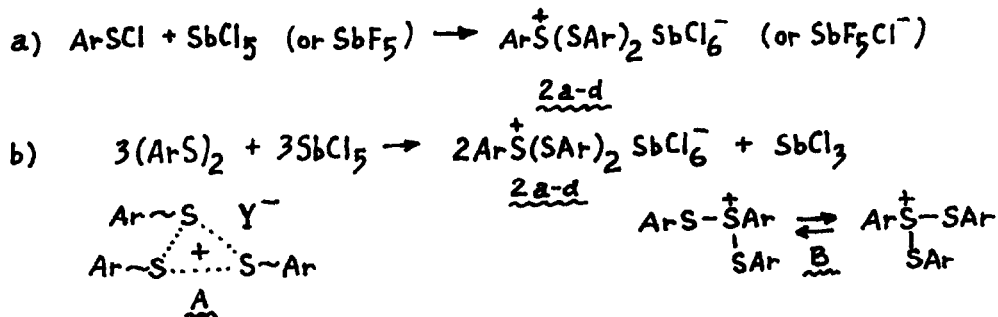
Summary: A new method for the preparation of S-arylepissulfonium salts has been developed and several compounds of this type have been isolated.

The most direct route to S-arylepissulfonium ions (S-aryl ESI's) involving the reaction of alkenes with cationoid reagents formally depicted as arylsulfonium salts ArS^+Y^- , 1, has been successfully used for the preparation of various S-aryl ESI's as the stable solutions¹. However the inherent instability of 1 has precluded their proper identification and made the whole procedure rather inconvenient.

Here we report: (i) the preparation of a new class of electrophilic reagents, aryl-bis(thioaryl)sulfonium salts, $ArS^+(SAr)_2 Y^-$, 2, $Ar=C_6H_5$ (a); $4-CH_3C_6H_4$ (b); $4-ClC_6H_4$ (c); $2,4,6-(CH_3)_3C_6H_2$ (d); $Y^- = SbCl_6$ or SbF_5Cl^- ; (ii) the effective use of these salts for the conversion of alkenes into their respective S-aryl ESI's and (iii) the first isolation of several S-aryl ESI's in a free state.

The preparation of 2a-d is achieved easily according to the reactions shown in Scheme 1³ by mixing of the equimolar quantities of the reagents dissolved in CH_2Cl_2 or liquid SO_2 at -60° . The reactions are complete in a few minutes⁴ and produce 2a-d quantitatively⁵.

Scheme 1



The coloured solution of 2a-d so prepared could be stored at -70° for at

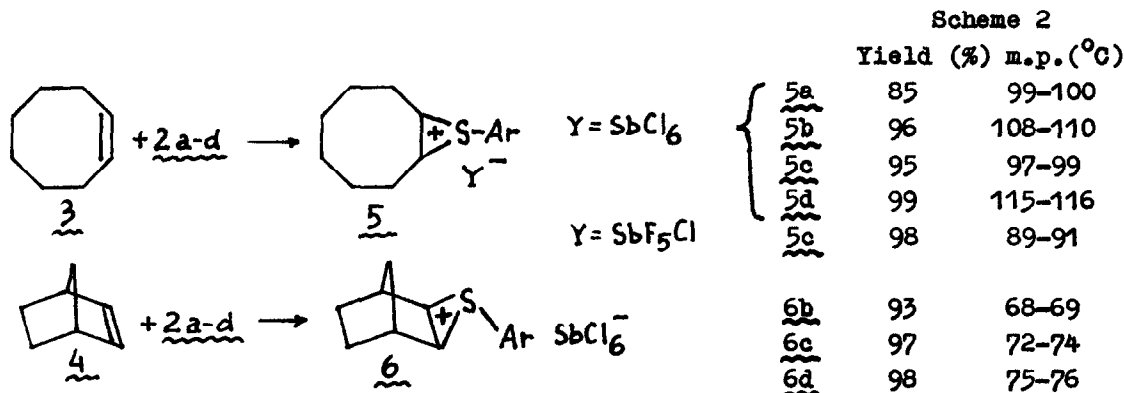
least several hours⁵; addition of cooled Et₂O allowed us to isolate salts 2c,d as solids in 50-60% yields⁵; however these salts proved to be rather unstable even at -20^o5.

A noteworthy feature of the CMR spectra of 2a-d at -60^o (see Table 1) is the appearance of a single set of ¹³C-aryl signals, their positions being indicative of the presence of a positively charged center adjacent to the aryl residue⁶. Such a pattern could be accounted for by postulation of a cyclic triaryltrithianium structure A for these compounds, or ascribed to averaging due to the rapid degenerate equilibration B (Scheme 1). At present the former alternative seems to be more plausible⁷ especially in view of the additional temperature-variable CMR studies⁸.

CMR-spectra of	<u>2a-d</u> [*]	¹³ C-1	¹³ C-2,6	¹³ C-3,5	¹³ C-4
Salt (aryl)					
<u>2a</u> (C ₆ H ₅)	124.3	136.7	132.7	136.7	
<u>2b</u> (4-CH ₃ C ₆ H ₄)	121.8	136.3	133.3	147.8	
<u>2c</u> (4-ClC ₆ H ₄)	122.0	137.5	132.1	142.3	
<u>2d</u> (2,4,6-(CH ₃) ₃ C ₆ H ₂)	123.4	146.4	132.8	148.4	

*Spectra were recorded at 15.08 MHz with Bruker WP-60 FT spectrometer for 0.7-0.8 M solutions in CH₂Cl₂ at -60^o; δ (ppm) are given relative to TMS (external).

The ability of 2a-d to serve as S-aryl transfer agents has been established by their reactions with cis-cyclooctene (3) and norbornene (4). For both alkenes the arylsulfenylation proceeds smoothly even at -60^o upon introduction of alkene into a solution of 2a-d (1:1 molar ratio). The resulting S-aryl ESI's 5 or 6 are easily isolated in a free state⁹ by addition of cooled Et₂O, followed by filtration under argon, additional washing with ether (to remove the traces of ArSSAr) and n-pentane and drying in vacuo.



Prior to this study no reports on the isolation of free S-aryl ESI's have appeared¹⁰.

The structure of ESI's 5 and 6 has been ascertained both by NMR data and the results of the quenching experiments. Thus PMR spectra of 5a-d and 6b-d

contain typical ^2H -signals of the $\text{CH}-\text{CH}$ fragment at 4.6-4.7 ppm (as multiplets for 5 and broadened singlets for 6)¹¹.

CMR studies with 5a-d and 6b-d ($\text{Y}^- = \text{SbCl}_6^-$) proved to be difficult due to their low solubility. Therefore more soluble ESI's have been prepared: 5d ($\text{Y}^- = \text{BF}_4^-$) and norbornene-*S*-methylepisulfonium salt, 7, ($\text{Y}^- = \text{SbF}_6^-$)¹². The CMR spectra¹³ of both these compounds contain only four ^{13}C -signals of cycloaliphatic carbons (for 5d: 77.0, 26.1, 26.2, 28.2; for 7: 63.1, 38.8, 25.2, 18.5) as should be the case for the plane symmetrical structure of these ESI's. The near-identity of PMR spectra of ESI's with various counter-ions ($\text{Y}^- = \text{BF}_4^-$, SbCl_6^- or SbF_5Cl^-) allows us to consider this conclusion as generally valid for the whole set of the prepared ESI's.

The quenching of all salts 5 and 6 with $(\text{CH}_3)_4\text{NOAc-AcOH}$ mixture proceeds in a manner usual with other ESI¹ and produces 1,2-acetoxy-arylthio-adducts as the major products (yields are 88-99% for 5 and 60-80% for 6)¹⁴.

This method of alkene arylsulfenylation seems to be of general value. Thus it was shown that interaction of 2d with such alkenes as 2,3-dimethyl-2-butene, cyclohexene, 1-methylcyclohexene and styrene produces the respective *S*-aryl ESI's as revealed by their ready conversion into the respective acetoxy-adducts (yields 70-90%) upon quenching with acetate anion^{14,15}.

We believe that the proposed simplified procedure for the preparation of *S*-aryl ESI's will greatly facilitate the elaboration of synthetically useful methods based on the well-documented ability of these compounds¹ to react as "masked" carbonium ion equivalents. Studies along these lines are now in progress.

References

1. a) E.A.Vorobieva, M.Z.Krimer, W.A.Smit, Izvestia Akad.Nauk, Ser.chim., 2832 (1974); b) W.A.Smit, M.Z.Krimer, E.A.Vorobieva, Tetrahedron Lett., 2451 (1975).
2. Reagents 1 have been generated in situ by the action of AgBF_4 or AgSbF_6 on ArSHal^1 . Earlier the formation of 1 as unstable electrophilic species has been suggested by N.Kharasch et al. (see, for example N.Kharasch, C.B. Buess, W.King, J.Amer.Chem.Soc., 75, 6035 (1953); see also D.Owsley, G.Helmkamp, J.Amer.Chem.Soc., 89, 4558 (1967) and references given therein).
3. These reactions are essentially similar to those described previously for the preparation of $\text{CH}_3\text{S}^+(\text{SCH}_3)_2\text{SbCl}_6^-$: a) G.Capozzi, C.Lucchini, G.Modena, F.Rivetti, J.Chem.Soc., Perkin II, 900 (1975); b) R.Weiss, C.Schliers, Synthesis, 323 (1976). To our knowledge no attempts have been made to apply these procedures to the synthesis of other *S*-alkyl- or *S*-aryl transferring reagents.
4. CMR spectra recorded 30 min after the mixing of the reagents indicated the absence of the signals of the starting compounds.

5. To determine the yields of 2a-d and to evaluate their stability the data on the yields of the respective S-aryl ESI's in the reactions with cis-cyclooctene were used.
6. In CMR spectra of 2a-d signals of $^{13}\text{C}-1$ are shifted 12-15 ppm upfield while those of $^{13}\text{C}-2,4,6$ are shifted 6-8 ppm downfield relative to the respective ^{13}C -signals in model uncharged compounds (ArSSAr , ArSCH_3).
7. While the formation of cyclic trithian has never been observed and the latter was considered to be unlikely formulation for the structure of $\text{CH}_3\text{S}^+(\text{SCH}_3)_2$ salt (see ref.3a), recent ab initio calculations of the model reaction $(\text{HS})_2 + \text{E}^+$ give some support for the feasibility of such bridged structure (J.A.Pappas, *J.Amer.Chem.Soc.*, 101, 561 (1979)).
8. CMR spectra of 2a-d recorded at -90° show the presence of a double set of closely similar ^{13}C -signals this phenomenon being interpreted as the result of the freezing out of syn-anti equilibration in A. More detailed discussion of the observed reversible changes will be given in a full paper.
9. All salts are isolated as finely crystalline powders with sharp m.p.'s (decomp.). They could be stored unchanged at least for several days at $+20^\circ$ (for 5a-d) or 0° (for 6b-d). Yields are given for the isolated compounds; satisfactorily analytical data were obtained for all salts.
10. Up to now only several stable S- CH_3 ESI's have been isolated (e.g.: G.Cappozzi, O.DeLucchi, G.Modena, *Tetrahedron Lett.*, 2063 (1975); P.Raynolds, Z.Zonnebelt, S.Bakker, R.M.Kellogg, *J.Amer.Chem.Soc.*, 96, 3146 (1974).
11. PMR spectra were recorded at 100 MHz with Tesla BS 497 spectrometer for CD_3CN solutions at -40° (for 5a-d) or $(\text{CD}_3)_2\text{CO}$ solutions at -95° (for 6b-d); δ (ppm) are given relative to TMS (internal). The respective signals of other protons are also observed in all the spectra.
12. These salts were prepared using previously described methods^{1b} and were isolated as analytically pure hygroscopic compounds in 40-50% yields.
13. CMR spectra were recorded at 15.08 MHz for CH_2Cl_2 solutions at $+20^\circ$; δ (ppm) are given relative to TMS (external).
14. Yields refer to the isolated products. Satisfactory analytical data were obtained for all adducts. The vicinal position of OAc and S-ar groups has been ascertained by the appropriate double-irradiation PMR experiments.
15. The isolation of S-aryl ESI in a free state was successful only for 2,3-dimethyl-2-butene (yield 84%, satisfactory analytical data).

(Received in UK 20 November 1979)