Investigations on the Lewis-acids-catalysed electrophilic aromatic substitution reactions of thionyl chloride and selenyl chloride, the substituent effects, and the reaction mechanisms

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The previously established aluminium-chloride-(AlCl₃)-catalysed electrophilic aromatic substitution (EAS) of benzene (PhH) with thionyl chloride (SOCl₂) has been extended to toluene (PhCH₃), chlorobenzene (PhCl), and phenol (PhOH). –CH₃ was found to be mainly a *para*-director with a minor *ortho*-directing effect on the EAS reactions giving diaryl sulfoxides (Ar₂SO). –CI was found to be exclusively a *para*-director for formation of Ar₂SO. All the –CH₃, –CI, and –OH groups were shown to be exclusive *para*-directors for formation of diaryl sulfides (Ar₂S) from the EAS reactions. Although the reactions of PhH and PhCH₃ with SOCl₂ in the presence of AlCl₃ gave the major Ar₂SO and minor Ar₂S at ambient temperature, the phenol (PhOH) reaction was shown to give only the reduced sulfide (*p*-HOC₆H₄)₂S with no sulfoxide (*p*-HOC₆H₄)₂SO formed. The mixed diaryl sulfoxides ArSOAr' (Ar, Ar'=C₆H₅, *p*-CH₃C₆H₄; C₆H₅, *o*-CH₃C₆H₄; and C₆H₅, *p*-ClC₆H₄) were produced in the AlCl₃-catalysed reactions of SOCl₂ with molar 1:1 PhH–PhX mixtures (X=CH₃ and Cl). Efforts to enhance the yield of *S*-aryl arenesulfonothioates ArSO₂SAr (Ar=Ph, *p*-CH₃C₆H₄, and *p*-ClC₆H₄) from the AlCl₃-catalysed EAS reactions of SOCl₂ were made, showing that decreasing the molar ratios of ArH/SOCl₂ or lowering the temperature resulted in an increase in the product yield. A detailed mechanism has been proposed to account for the formation of ArSO₂SAr. The Lewis-acid-MCl₃-(M=Al and Fe)-catalysed EAS reactions of PhH with selenyl chloride (SeOCl₂) were demonstrated to give the reduced diphenyl selenide (Ph₂Se) and diphenyl diselenide (PhSeSePh) *via* novel auto-redox processes in selenium of the key EAS intermediates.

Keywords: organosulfur, organoselenium, auto-redox, aromatic, CH substitution, functionalisation

Diaryl sulfoxides (Ar,SO), parented by Ph,SO, are valuable reagents in organic chemistry1 and have found substantial utility in synthetic and biomedical applications. For example, $Ar_{3}SO(Ar=Ph and m-CF_{3}C_{6}H_{4})$ have been used in carbohydrate synthesis to facilitate the formation of glycosidic bonds.² Ph₂SO has been used effectively in the catalytic oxidation of various alkyl sulfides (RSR') to sulfoxides (RSOR').3 In medicinal chemistry, diaryl sulfoxides [Ar=Ph, p-O2NC6H4, p-H2NC6H4, and p-(ClCH₂CH₂)₂NC₆H₄] have been used as precursors to anti-cancer drugs.^{4,5} Usually, diaryl sulfoxides, including diphenyl sulfoxide Ph₂SO, are made by catalytic oxidation of the corresponding diaryl sulfide Ar₂S.^{6,7} The preparation involves complicated transition-metal-complex based catalysts. It often suffers with over-oxidation to diaryl sulfone (Ar₂SO₂) side products. Particularly, preparation of the starting Ar_sS is tedious and often requires sophisticated catalysts as well.8-10 Some diaryl sulfoxides were made by reaction of aryl O-menthyl sulfoxide with ArMgX (Grignard reagent).11 Obviously, many efforts must be made in preparing the starting materials prior to synthesis of the targeted Ar₂SO.

Very often, functionalisation of aromatic hydrocarbons can be readily achieved by electrophilic aromatic substitution (EAS) reactions in which an aromatic C–H bond reacts *via* a Wheland intermediate (σ -complex), and the hydrogen is replaced by an electrophile.^{12,13} Following this approach, Olah and Nishimura¹⁴ studied the AlCl₃-catalysed EAS reactions of benzene and toluene with arenesulfinyl chlorides (ArSOCI). The reactions gave various diaryl sulfoxides (but purity and yields unreported) at 25 °C. Recently, we have conducted the aluminium-chloride-(AlCl₃)-catalysed Friedel–Crafts (EAS) reactions of thionyl chloride (SOCl₂) with benzene (PhH).¹⁵ Under certain conditions (such as adding SOCl₂ slowly to the PhH–AlCl₃ mixture at 25 °C to keep PhH in excess during the reaction), we were able to make pure (99.9%) Ph₂SO in good yields (~80%). Formation of Ph₂SO was demonstrated to take place by the following double consecutive EAS reactions [Eqn (1)].¹⁵ (1)

$$2 \text{ PhH} + \bigcup_{Cl} S \underbrace{\text{AlCl}_3}_{Cl} \left[\text{PhH} + \bigcup_{Ph} S \underbrace{\text{Cl}}_{l} + \text{HCl} \right] \underbrace{\text{AlCl}_3}_{Ph} \underbrace{\text{Ph}}_{S} \underbrace{\text{Ph}}_{Ph} + 2 \text{HCl}$$

As the temperature and the manner of mixing starting materials varied, Ph_2S was produced from the reaction in significant yields together with formation of $PhSO_2SPh$ (~5%) and $PhSO_2Ph$ (trace). Formation of these aromatic organosulfur compounds was unexpected and involved a very interesting oxidation–reduction (redox) process in the sulfur centre. The possible mechanisms were presented.¹⁵

In the present work, we extend our investigations on this type of EAS reaction to substituted benzenes, including toluene (PhCH₂), chlorobenzene (PhCl), and phenol (PhOH). We now emphasise studies of the substituent effects of -CH₃₂ -Cl, and -OH on the regiochemistry (directing effects) as well as the effects on the redox chemistry occurring in the sulfur centre during the reactions. The current studies are also extended to formation of the mixed diaryl sulfoxides XC₆H₄SOPh (X=CH₃ and Cl) from the AlCl,-catalysed EAS reactions of SOCl, and the directing effects of the substituents (-CH₃ and -Cl) on the reactions. In addition, we report our attempt on enhancing the yields of S-aryl arenesulfonothioate ArSO₂SAr (Ar=C₆H₅, p-CH₂C₆H₄, and p-ClC₆H₄) produced from the AlCl₂-catalysed EAS reactions of SOCl₂. Directing effects of -CH₃ and -Cl on formation of ArSO₂SAr are discussed. A reaction mechanism involving more detailed molecular interactions is proposed.

Finally, we have extended our studies to the Lewis-acid- MCl_3 -(M=A1 and Fe)-catalysed electrophilic substitution reactions of benzene with selenyl chloride (SeOCl₂), the selenium analogue of SOCl₂. Substantially different behaviour of SeOCl₂ from that of SOCl₂ has been discovered. The reaction has been surprisingly found to give diphenyl selenide (Ph₂Se) and diphenyl diselenide (PhSeSePh). Possible mechanisms for these novel reactions are discussed in this work. Ph₂Se and PhSeSePh have many applications in organic synthesis and they are usually prepared by complicated approaches.¹⁶

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$2PhX + SOCl_2 - A$			X X + € S +		+ x C - S C x			
X=CI	89%	0	0	0	11%	0		
X=CH ₃	55%	34%	11%	0	0	0		
socl ₂ added dropwise to the PhX/AICl ₃ mixture at 25 °C								
X=CI	100% ^b	0	0	0	0	0		
X=CH ₂	50%	26%	4%	4%	0	16%		
[°] AICl ₃ added to the PhX/SOCl ₂ mixture piecewise at 25 °C								
X=CI	39%	7%	0	51%	3%	0		
X=CH ₃	58%	27%	8%	7%	0	0		
AICI ₃ added to the PhX/SOCI ₂ mixture piecewise at 70 °C								

Table 1 Distribution of products formed in the AICl₃-catalysed reactions of PhX (X=Cl and CH₃) with SOCl₂ in the molar ratio of PhX:SOCl₃:AICl₃=2:1:1^a

^aAll the percentages are relative normalised yields, estimated by comparison of areas of the GC spectra of related components, assuming that the peak area is proportional to the number of moles of the component. The assumption is supported by the established analogous relationship for the Ph₂Se–PhSeSePh system, Eqn (8) in the experimental section.

^bA sole component of $(p-\text{CIC}_6\text{H}_4)_2$ SO was formed based on GC–MS analysis. Its absolute (isolated) percent yield was determined to be 71% by comparison of the actually recovered mass of the product with the theoretical yield.

Results and discussion

Substituent effects on the $AlCl_3$ -catalysed electrophilic aromatic substitution reactions of SOCl,

Analogous to the benzene reaction,¹⁵ when SOCl₂ was added slowly (dropwise) to the PhCH₂-AlCl₂ mixture (to keep PhCH₂) in excess) at 25 °C, the reaction only gave the diaryl sulfoxide isomers (p-CH₃C₆H₄),SO (55%), p-CH₃C₆H₄SO(o-CH₃C₆H₄) (34%), and $(o-CH_2C_2H_4)_2SO$ (11%) (Table 1). No other organosulfur compounds were produced. This shows the methyl group is mainly a para-director with a minor ortho-directing effect on the type of EAS reactions leading to diaryl sulfoxides. Such a directing effect has also been revealed from the toluene reactions under different conditions in Table 1, which gave the major diaryl sulfoxide isomers together with small percentages of other organosulfur compounds. In many other EAS reactions of toluene (such as halogenation, nitration, and Friedel-Crafts alkylation), the -CH₃ group is approximately an equal paraand ortho-director.^{12,13,16} However, in the EAS product with SOCl,, the sulfoxide S=O group may produce substantial steric hindrance on its ortho-carbon, making the -CH₃ group a major para-director. Similarly, the AlCl₂-catalysed reaction of p-CH₂C₄H₄SO₂Cl with toluene has been reported to give 80% $(p-CH_3C_6H_4)$, \tilde{SO}_2 and only 20% $p-CH_3C_6H_4SO_2(o-CH_3C_6H_4)$.¹⁷

When AlCl₃ was added slowly (piecewise) to the PhCl– SOCl₂ mixture (to keep PhCl in excess over the reactive SOCl₂–AlCl₃ adduct) at 25 °C, the reaction led to formation of a sole sulfoxide isomer (p-ClC₆H₄)₂SO (Table 1), showing the –Cl group is essentially only a *para*-director for formation of the diaryl sulfoxide. No other organosulfur compounds were formed. The *para*-directing effect is mainly due to conjugation of the lone-pair of electrons in –Cl.^{12,13,16} In addition, the lack of the *ortho*-isomer of sulfoxide in most of the PhCl reactions may be attributable to the repulsions between the –Cl electron pairs and the electron pairs in the S=O group of the transition state leading to the *ortho*-isomer (o-ClC₆H₄)₂SO.

Our previous work showed that when AlCl₃ was added piecewise to the PhH–SOCl, mixture at 70 °C, the reaction gave

only the sulfoxide Ph₂SO with no reduced sulfide Ph₂S formed.¹⁵ Similarly, Table 1 shows that the toluene reaction under the same conditions gave mainly diaryl sulfoxide isomers, with only very minor sulfide (*p*-CH₃C₆H₄)₂S (7%) produced. However, the PhCl reaction at 70 °C, with AlCl₃ added piecewise to the PhCl–SOCl₂ mixture, resulted in formation of the major diaryl sulfide (*p*-ClC₆H₄)₂S (51%) (the only observed sulfide isomer) together with minor sulfoxide isomers (*p*-ClC₆H₄)₂SO (39%) and *p*-ClC₆H₄SO(*o*-ClC₆H₄) (7%). This demonstrates that –Cl and – CH₃ possess substantially different effects on redox chemistry of the sulfur centre, leading to different product distributions. Such difference in the effects on the redox chemistry possessed by the two substituent groups can also be seen by comparison of the product distributions of the reactions in Table 1 under other conditions.

The substituent effect on the redox chemistry of the sulfur centre associated to the AlCl₂-catalysed EAS reactions of SOCl₂ is further demonstrated by examining the reaction of phenol (PhOH). The experimental results (Table 2) show that quick addition of PhOH to the SOCl2-AlCl3 mixture at 25 °C gave 91% $(p-HOC_6H_4)_2$ S and 9% $p-CIC_6H_4OH$, while slow (piecewise) addition of AlCl, to the PhOH-SOCl, mixture at 25 °C gave $51\% (p-HOC_6H_4)$, S and $49\% p-ClC_6H_4OH$. Different from PhX (X=H, CH₂, and Cl) whose reactions with SOCl₂ in the presence of AlCl, at 25 °C always gave the major Ar₂SO and minor Ar₂S, the AlCl₃-catalysed reactions of PhOH with SOCl₂ at 25 °C only gave the reduced bis(p-hydrophenyl) sulfide $(p-HOC_6H_4)_2S$, together with the minor p-chlorophenol (p-ClC₄H₄OH) side product. The initially expected diaryl sulfoxide $(p-HOC_{e}H_{a})_{2}SO$ or any other sulfoxide isomers (on the basis of the reactions of other arenes) were not found from the reaction product. No other organosulfur compounds were formed. The -OH group is exclusively a para-director for the AlCl₃-catalysed EAS reactions of SOCl, giving the diaryl sulfide. Different from the -CH₂ and -Cl groups, the strongly activating -OH facilitates the complete reduction of S(IV) in SOCl₂ to S(II) in $(p-HOC_6H_4)_2S$ in the course of the EAS reaction.

Table 2 Product yields (normalised molar percentages) for the AICl₃-catalysed reactions of phenol (PhOH) and thionyl chloride (SOCl₂) with the molar PhOH:SOCl₂:AICl₃=2:1:1 under different conditions

t∕°C	Manner of mixing	$(p-HOC_6H_4)_2S$	<i>p</i> -HOC ₆ H ₄ Cl	$(p-HOC_{6}H_{4})_{2}SO$
25	PhOH/ether solution added all at once to the AICl ₃ –SOCl ₂ mixture	91%	9%	0
25	AICl ₃ added piecewise to the PhOH–SOCl ₂ mixture	51%	49%	0

We believe that common to all the arenes, the first step of the $AlCl_3$ -catalysed reaction of PhOH with $SOCl_2$ is the aromatic C–H bond substitution by $SOCl_2$ giving *p*-HOC₆H₄SOCl–AlCl₃ (the AlCl₃ adduct of the first EAS intermediate) [Eqn (2)].

$$HO \longrightarrow S_{Cl} \xrightarrow{e} HO \xrightarrow{AlCl_3} HO \xrightarrow{AlCl_3}$$

The electron-donating –OH on the *para*-carbon of p-HOC₆H₄SOCl–AlCl₃ can possibly decrease the electrophilicity of the sulfur centre by delocalising the positive charge from S=O⁺– to the –OH oxygen by conjugation as shown in Eqn (2). As a result, the sulfur centre in *p*-HOC₆H₄SOCl–ACl₃ was unreactive towards an aromatic ring. Therefore, the rate of the second EAS reaction of *p*-HOC₆H₄SOCl–AlCl₃ with PhOH was significantly reduced and the corresponding sulfoxide (*p*-HOC₆H₄)₂SO (or any other sulfoxide isomers) were not formed. Instead, after the *p*-HOC₆H₄SOCl–AlCl₃ intermediate was produced, it underwent an exclusive intramolecular autoredox reaction [Eqn (3)], the mechanism of which is analogous to that for the formation of Ph₂S from the benzene reaction.¹⁵



In the presence of AlCl₃, a small fraction of phenol in the reaction mixture reacted readily with Cl₂, produced from the intramolecular auto-redox and experimentally identified, to give *p*-chlorophenol (*p*-ClC₆H₄OH) as a minor side product. When AlCl₃ was added slowly (piecewise) to the PhOH–SOCl₂ mixture, PhOH remained in excess. Therefore, the amount of *p*-ClC₆H₄OH formed was much greater than that produced from the reaction by adding PhOH quickly to the SOCl₂–AlCl₃ mixture. Formation of *p*-ClC₆H₄OH in the reaction has provided further support for the previously proposed intramolecular redox process (which gives off Cl₂)¹⁵ involved in the reaction mechanism.

Our study showed that in contrast to the toluene reactions at 25 °C which always gave the major sulfoxide and minor sulfide products (Table 1), the AlCl₃-catalysed reaction of pentamethylbenzene $[C_6H(CH_3)_5]$ with SOCl₂ at 25 °C [conducted by adding $C_6H(CH_3)_5$ to the SOCl₂-AlCl₃ mixture] gave a sole reduced di(pentamethylphenyl) sulfide $[C_6(CH_3)_5]_2$ S product (GC-MS), while the corresponding di(pentamethylphenyl) sulfoxide $[C_6(CH_3)_5]_2$ SO was not formed. The five electron-donating methyl groups can effectively decrease the electrophilicity of the sulfur centre in the first EAS intermediate $C_6(CH_3)_5$ SOCl-AlCl₃. As a result, the EAS of a second $C_6H(CH_3)_5$ molecule with $C_6(CH_3)_5SOCI-AlCl_3$ could not happen to give $[C_6(CH_3)_5]_2SO$. Instead, an intramolecular auto-redox process occurred to $C_6(CH_3)_5SOCI-AlCl_3$ exclusively [see Eqn (3)] to lead to formation of the sulfide $[C_6(CH_3)_5]_2S$ as a sole product.

Formation of the mixed diaryl sulfoxides p-XC₆H₄SOPh (X=CH₃ and Cl)

The AlCl₃-catalysed reactions of SOCl₂ with the molar 1:1 mixtures of PhH–PhX (X=CH₃ and Cl) were performed at 25 °C, with AlCl₃ added slowly (piecewise) to the PhH–PhX–SOCl₂ mixtures. Essentially, reactions of both PhH–PhX mixtures gave diaryl sulfoxides. Mixed diaryl sulfoxides p-XC₆H₄SOPh (X=CH₃ or Cl) and o-XC₆H₄SOPh (X=CH₃) were produced in each reaction, in addition to formation of Ph₂SO and (p-XC₆H₄)₂SO (Table 3).

As shown in Fig. 1, SOCl₂ is believed to react with both PhH and PhX (X=CH₃ or Cl) separately to give PhSOCl and XC₆H₄SOCl (*para-* or *ortho*) in the first step. Then reaction of PhSOCl with PhX or reaction of *p-*XC₆H₄SOCl with PhH took place to lead to formation of the mixed diaryl sulfoxide *p-*XC₆H₄SOPh and *o-*XC₆H₄SOPh, while reaction of PhSOCl with PhH gave Ph₂SO and reaction of XC₆H₄SOCl with PhX gave (*p-*XC₆H₄)₂SO (X=Cl or CH₃), *p-*XC₆H₄SO(*o-*XC₆H₄)(X=CH₃), and (*o-*XC₆H₄)₂SO (X=CH₃). The observed directing effects of $-CH_3$ and -Cl on the reactions giving the mixed diaryl sulfoxides *p-*XC₆H₄SOPh and *o-*XC₆H₄SOPh (Table 3) are consistent with those on the reactions in Table 1, namely that $-CH_3$ is mainly a *para-*director with minor *ortho-*directing effect on formation of diaryl sulfoxide, while -Cl is an exclusive *para-*director.

Relatively, the percentage of the mixed p-ClC₆H₄SOPh (43%) was higher than the total percentage (39%) of the mixed p-CH₃C₆H₄SOPh (33%) and p-CH₃C₆H₄SOPh (6%) (Table 3). This is likely because the electron-withdrawing –Cl group in the intermediate p-ClC₆H₄SOCl enhances the electrophilicity of the sulfur centre, making p-ClC₆H₄SOCl more reactive than PhSOCl and p-CH₃C₆H₄SOCl. Formation of the mixed diaryl sulfoxides p-XC₆H₄SOPh (X=CH₃ and Cl) provided further evidence to support the mechanism for the AlCl₃-catalysed double consecutive EAS reactions of SOCl₂ [Eqn (1)].

Enhancing yields for formation of S-aryl arenesulfonothioates $ArSO_2SAr$ (Ar=Ph, $p-CH_3C_6H_4$, and $p-ClC_6H_4$) and directing effects of substituents on the reactions

Our previous work indicated that the AlCl₃-catalysed reactions of benzene with SOCl₂ very often gave a very small amount of PhSO₂SPh (only~5%)¹⁵ in addition to formation of Ph₂SO and Ph₂S in more appreciable yields. Formation of PhSO₂SPh in the EAS reaction, although in a very low yield, was still considered mechanistically interesting. Since then, we have made substantial efforts to optimise the conditions

Table 3 The relative normalised yields of products for the AICl₃ catalysed reactions of $SOCl_2$ with the molar 1:1 mixtures of PhH and PhX (X=CH₃ and Cl)^a

$PhH + PhX + SOCl_2 $ AlCl						
X=CI	28%	43%	0	29%	0	0
X=CH ₃	16%	33%	6%	32%	10%	2%

^aAll the percentages are relative normalised yields, estimated by comparison of areas of the GC spectra of related components, assuming that the peak area is proportional to the number of moles of the component. The assumption is supported by the established analogous relationship for the Ph₂Se–PhSeSePh system, Eqn (8) in the experimental section.

Formation of ArSOCI

PhX + SOCl₂
$$\xrightarrow{AlCl_3}$$
 \xrightarrow{X} \xrightarrow{Cl} \xrightarrow{Cl} + \xrightarrow{X} \xrightarrow{O} Cl
X = CH₃ or Cl X = CH₃
PhH + SOCl₂ $\xrightarrow{AlCl_3}$ Ph \xrightarrow{O} Cl

Formation of ArSOAr' (mixed diaryl sulfoxide)



Formation of ArSOAr



Fig. 1 Mechanistic steps for the AICl₃-catalysed reactions of SOCl₂ with the molar 1:1 mixtures of PhH and PhX (X=CH₃ and CI): Formations of the mixed diaryl sulfoxides ArSOAr'.

for PhSO₂SPh formation and to enhance its yield in order to reinforce the proposed mechanism.¹⁵ We have found in this work that the yield of PhSO₂SPh can be greatly enhanced by slowly (dropwise) adding PhH to the SOCl₂–AlCl₃ mixture (to keep PhH in deficit). The yield can also be enhanced by lowering the temperature. Eqn (4) shows the results for the AlCl₃-catalysed reactions of benzene and SOCl₂ in the molar ratio of PhH:SOCl₂:AlCl₃ = 1:1:1, with benzene dropwise added to the SOCl₂–AlCl₃ mixture at 0 °C and –10 °C, respectively.

At -10 °C the reaction gave the major PhSO₂SPh (49%), together with the minor Ph₂SO (36%) and Ph₂S (15%). The yield of PhSO₂SPh at -10 °C (49%) was significantly higher than that at 0 °C (36%).

We have also extended the reactions under the same conditions (dropwise adding the arene to the SOCl₂–AlCl₃ mixture at 0 °C or –10 °C) to toluene and chlorobenzene. The reaction of toluene (PhCH₃) [Eqn (5)] gave 30% *p*-CH₃C₆H₄SO₂S(*p*-CH₃C₆H₄) (the only observed *S*-aryl arenesulfonothioate isomer), together with (*p*-CH₃C₆H₄)₂S (25%) (the only observed diaryl sulfide isomer), (*p*-CH₃C₆H₄)₂SO (35%), and *p*-CH₃C₆H₄SO(*o*-CH₃C₆H₄) (10%). Eqn (5) shows that –CH, is an exclusive *para*-director for

formation of the S-aryl arenesul fonothioate $[p-CH_3C_6H_4SO_5S(p-CH_3C_6H_3C(p-CH_3C_6H_3SO_5S(p-CH_3C_6H_3C(p-CH_3C_6H_3CO_5S(p-CH_3C_6H_3SO_5S(p-CH_3C_6H_3C($

 $CH_3C_6H_4$] and diaryl sulfide [$(p-CH_3C_6H_4)_2S$], while it functions as *para*- and *ortho*-directors for formation of the diaryl sulfoxide isomers. The *ortho*-isomers of arenesulfonothioate and sulfide were not identified from the reaction. Comparison of Eqn (4) and Eqn (5) indicates that under the same conditions (-10 °C), the benzene reaction gave a significantly higher yield of *S*-aryl arenesulfonothioate (49%) than did the toluene reaction (30%).

The reactions of chlorobenzene gave three organosulfur compounds. Their identities and yields are shown in Eqn (6).

40% p-ClC₆H₄SO₂S(p-ClC₆H₄) and 33% p-ClC₆H₄SO₂S(p-ClC₆H₄) were produced in the reactions with the PhCl:SOCl₂:AlCl₃ molar ratios of 1:2:2 and 1:1:1 respectively. This indicates that lowering the PhCl/SOCl₂ ratio (from 1:1 to 1:2) facilitated formation of the *S*-aryl arenesulfonothioate. For each organosulfur compound, only the *para*-isomer was found. The –Cl group functions as an exclusive *para*-director for formation of all the aromatic organosulfur compounds in Eqn (6).

In our previous work,¹⁵ we thought the formation of very minor PhSO₂SPh (~5%) in the AlCl₃-catalysed EAS reactions of PhH with SOCl₂ possibly resulted from an oxygen exchange between two molecules of the AlCl₃ adduct of the initially formed EAS intermediate (ArSOCl–AlCl₃). We now propose more detailed molecular interactions to account for the AlCl₃-catalysed oxygen exchange and subsequent transformations involved in the formation of *S*-aryl arenesulfonothioates ArSO₂SAr (Ar=C₆H₅, *p*-CH₃C₆H₄, and *p*-ClC₆H₄) in significant yields (Fig. 2). The nucleophilic sulfur (due to a lone-pair of electrons) in one ArSOCl–AlCl₃ molecule could possibly



attack the electrophilic oxygen in another in a nucleophilic displacement reaction. This results in cleavage of an oxygen–sulfur bond and transfer of the oxygen atom from one molecule to another, giving ArSO₂Cl–AlCl₃ [S(VI)] and ArSCl [S(II)] (Fig. 2). In the following step, the nucleophilic sulfur(II) in ArSCl attacks the electrophilic sulfur(VI) in ArSO₂Cl–AlCl₃, resulting in formation of ArSO₂SAr [containing an S(VI)–S(II) linkage] after aqueous work-up.

Formation of diphenyl selenide (Ph₂Se) and diphenyl diselenide (PhSeSePh) from the Lewis- acid- MCl_3 -(M=Al and Fe)-catalysed electrophilic substitution reactions of benzene (PhH) with selenyl chloride (SeOCl₂) and the accompanying auto-redox processes at the selenium centres of EAS intermediates

Following investigations of the AlCl₃-catalysed EAS reactions of SOCl₂, we have conducted the Lewis-acid-MCl₃-(M=Al and Fe)-catalysed electrophilic substitution reactions of benzene

(PhH) with selenyl chloride (SeOCl₂), the selenium analogue of SOCl₂. For each of the catalysts, the reaction was conducted by adding MCl₃ (M=Al or Fe) slowly to a PhH–SOCl₂ mixture at 25 °C, with the molar ratio of PhH:SOCl₂:MCl₃=2:1:1. The reactions catalysed by AlCl₃ and FeCl₃ gave 57% Ph₂Se and 43% PhSeSePh, and 40% Ph₂Se and 60% PhSeSePh, respectively (normalised yields in molar percentages) [Eqn (7)].

PhH + SeOCl₂
$$\xrightarrow{25 \text{ °C}}$$
 Ph₂Se + PhSeSePh
AlCl₃ 57% 43% (7)
FeCl₂ 40% 60%

No other organoselenium compounds, including the initially expected Ph₂SeO (diphenyl selenoxide) (on the basis of the SOCl₂ reaction), were identified from the products.



Fig. 2 The AICl₃-catalysed oxygen exchange between the ArSOCI–AICl₃ (Ar= C_6H_5 , *p*-CIC₆H₄, or *p*-CH₃C₆H₄) adduct molecules leading to formation of *S*-aryl arenesulfonothioate (ArSO₂SAr): A detailed mechanism.

Our previous work showed¹⁵ that under the same conditions, the AlCl₃-catalysed reaction of benzene with SOCl₂ gave the major Ph₂SO, together with the minor Ph₂S, PhSO₂SPh, and Ph₂SO₂, while diphenyl disulfide PhSSPh (the sulfur analogue of PhSeSePh) was not formed in the AlCl₃-catalysed reactions of benzene with SOCl₂ under any conditions. Clearly, the EAS reaction of SeOCl₂ is substantially different than the reaction of SOCl₂. The selenium atom in SeOCl₂ is substantially less electrophilic than the sulfur atom in SOCl₂ due to the greater polarisability of selenium than sulfur. This is consistent with the observation that the AlCl₃-catalysed reaction of benzene with SeOCl₂ was much slower than the reaction with SOCl₂ under the same conditions. We believe that the difference in the reactivity of SeOCl₂ and SOCl₂ towards benzene is primarily due to the greater polarisability of selenium than sulfur.

Fig. 3 shows the possible mechanism for the MCl₃-(M=Al and Fe)-catalysed reaction of PhH with SeOCl₂. Conceivably, SeOCl₂ and MCl₃ (M=Al or Fe) form an SeOCl₂-MCl₃ adduct, analogous to SOCl₂-AlCl₃.^{18,19} PhH is believed to undergo a similar EAS reaction with the SeOCl₂-MCl₃ adduct (much slower than the reaction with SOCl₂-AlCl₃) to form PhSeOCl-MCl₃. The electron-donating –Ph group in PhSeOCl-MCl₃ can further decrease the electrophilicity of the selenium centre. As a result, PhSeOCl-MCl₃ does not react with a second

benzene molecule to give Ph,SeO. Instead, it undergoes an exclusive intramolecular auto-redox process, analogous to that for p-HOC₆H₄SOCl-AlCl₃ [Eqn (3)], and Se(IV) in PhSeOCl-MCl, was reduced to Se(II) in PhSeO-MCl, (Fig. 3). The proposed auto-redox process is supported by identification of Cl₂ from the reaction mixture (using wet KI-starch paper, see the Experimental section). Similar to HOC, H₄SO-AlCl₂ [Eqn (3)], the selenium atom in PhSeO-MCl, could be attacked by a second benzene molecule to lead to formation of Ph₂Se (Fig. 3). On the other hand, the selenium centre in PhSeO-MCl₂, with a lone-pair of electrons, is fairly nucleophilic due to its relatively large polarisability. Therefore, it could effectively attack the selenium atom in a second PhSeO-MCl, molecule concurrently, leading to formation of a Se-Se bond and cleavage of a Se-O bond. The subsequent cleavage of the second Se⁺–O bond was facilitated by the positive charge on selenium. This eventually resulted in formation of PhSeSePh (Fig. 3). In the FeCl₃-catalysed reaction, the d_{π} orbital in Fe(III) in the PhSeO-FeCl, adduct might donate electron density to selenium by a $d_{\pi} - p_{\pi}$ back bonding, making the selenium centre more nucleophilic than that of PhSeO-AlCl₂. This may account for the fact that the FeCl₃-catalysed reaction of benzene with SeOCl, produced a significantly greater percentage (60%) of PhSeSePh than did the AlCl₃-catalysed reaction (43%).



Formation of diphenyl selenide (Ph₂Se):



Formation of diphenyl diselenide (PhSeSePh):



Fig. 3 Mechanism for the Lewis-acid-MCl₃-(M=Al and Fe)-catalysed electrophilic substitution of benzene (PhH) with selenyl chloride (SeOCl₂) giving diphenyl selenide (Ph₂Se) and diphenyl disefenide (PhSeSePh).

Conclusions

In this work, the previously established AlCl₃-catalysed EAS reaction of benzene with SOCl, possibly giving Ph2SO, Ph,S, and PhSO,SPh in various yields¹⁵ has been extended to other substituted benzenes, including PhCH₃, PhCl, and PhOH. The substituent effects of -CH₃, -Cl, and -OH on the regiochemistry of the reactions (directing effects) and the effects on the redox chemistry of the sulfur centre in the reactions have been studied. -CH₃ was found to be mainly a para-director with minor ortho-directing effect on formation of diaryl sulfoxide (Ar,SO) from the EAS reaction. However, it is an exclusive para-director for formation of diaryl sulfide (Ar₂S). On the other hand, -Cl and -OH are exclusively para-directors for formation of all the aromatic organosulfur compounds. The -CH₂, -Cl, and -OH groups were found to possess different effects on the redox chemistry of the sulfur centre in SOCl, during the EAS reactions, leading to different product distributions (percentages) under comparable reaction conditions. The difference in the effects on the redox chemistry is particularly remarkable on comparing the PhOH reaction with the reactions of PhX (X=H and CH₃). Although the AlCl₃-catalysed EAS reactions of benzene and toluene with SOCI, give the major diaryl sulfoxides with minor reduced diaryl sulfides,¹⁵ the reaction of PhOH at ambient temperature has been shown in this work to give only the reduced sulfide $(p-HOC_{a}H_{a})$ S (together with the minor p-chlorophenol side product). The corresponding sulfoxide $(p-HOC_6H_4)_2SO$ or any other sulfoxide isomers are not formed. This special reactivity of phenol is attributable to the conjugation of -OH, which lowers the electrophilicity of the sulfur centre in the first EAS intermediate p-HOC₆H₄SOCl-AlCl₃ to make it unreactive towards an aromatic ring. Instead, an exclusive intramolecular auto-redox occurs to lead to the formation of a diaryl sulfide [Eqn (3)].

It has been shown in this work that in the presence of AlCl₃, SOCl₂ can undergo double consecutive EAS reactions with two different arene molecules to give a mixed diaryl sulfoxide XC_6H_4SOPh (X=CH₃ or Cl). The directing effects of -CH₃ and -Cl on formation of XC_6H_4SOPh are consistent with those on the EAS reactions leading to diaryl sulfoxides Ar₂SO, namely, that -CH₃ is mainly a *para*-director with minor *ortho*-directing effect, and -Cl is exclusively a *para*-director for formations of XC_6H_4SOPh .

Our previous work indicated that the AlCl₂-catalysed reactions of benzene with SOCl, under many conditions gave a very small amount of PhSO₂SPh (only~5%).¹⁵ In this work, optimisation in reaction conditions has been attempted so that the yields of ArSO₂SAr (Ar=Ph, p-CH₂C₂H₂, and p-ClC₆H₄) have been enhanced up to (40–50)% (e.g. dropwise addition of PhH to the SOCl₂-AlCl₃ mixture at -10 °C gave PhSO₂SPh in 49% yield). Our studies have shown that in general decreasing the molar ratio of ArH/SOCl, or lowering the reaction temperature results in enhancement of the yield for formation of S-aryl arenesulfonothioate (ArSO₂SAr) from the AlCl₂-catalysed EAS reaction of SOCl₂. Both -CH₂ and -Cl were shown to be exclusive para-directors for formations of ArSO₂SAr. A mechanism with detailed molecular interactions has been proposed in this work to account for formations of ArSO₂SAr (Ar=Ph, p-CH₃C₆H₄, and p-ClC₆H₄) in significant yields via an AlCl₃-catalysed oxygen exchange between two EAS intermediate ArSOCI-AlCl₂ molecules.

The Lewis-acid-MCl₃-(M=Al and Fe)-catalysed Friedel– Crafts (EAS) reactions of benzene (PhH) with selenyl chloride (SeOCl₂), the selenium analogue of SOCl₂, have been shown in this work to give the reduced diphenyl selenide (Ph₂Se) and diphenyl diselenide (PhSeSePh). To our surprise, the initially expected diphenyl selenoxide (Ph_2SeO) was not produced at all in the reaction. A mechanism involving novel auto-redox processes in selenium has been proposed to account for the reactivity of SeOCl₂ towards aromatic hydrocarbons. This work has furnished the classical chemistry of aromatic compounds with novel aspects.

Experimental

Chemical reagents

Thionyl chloride $(SOCl_2)$ (purified) from J. T. Baker Chemical Company was used. Benzene (PhH) (99.9%), toluene (PhCH₃) (99.9%), chlorobenzene (PhCl) (99%), pentamethylbenzene $[C_6H(CH_3)_5]$ (99%), and phenol (PhOH) (99%) were obtained from Sigma Aldrich. Granular anhydrous aluminium chloride (AlCl₃) (99%, extra pure) was obtained from Acros Organics. Anhydrous sodium sulfate (99.5%, drying agent), dichloromethane (99.9%, the solvent for GC-MS samples), diethyl ether (solvent), selenyl chloride (SeOCl₂) (99%), and iron (III) chloride (FeCl₃) (98%) were purchased from Fisher Scientific Company.

The GC-MS measurements

Reaction products were identified using a Varian CP-3800 gas chromatograph-Varian Saturn 2200 mass spectrometer. The sample of each product was prepared by dissolving the product in dichloromethane to make the mass percentage of the product in the solution approximately 1%. One-microlitre of the solution was injected onto a Chrompack CP-SIL 8-CB 30m×0.25mm capillary column using a He carrier gas of 1.0 mL min⁻¹, a 1/100 injection split ratio, and a temperature ramp of 150 to 240 °C (10 °C min⁻¹). All chemical compounds were eluted in 10 minutes. The individual compounds (components) contained in each product, including Ar,SO $(Ar=p-CH_3C_6H_4, o-CH_3C_6H_4, p-ClC_6H_4), Ar_3S [Ar=p-CH_3C_6H_4, o-CH_3C_6H_4]$ p-ClC₆H₄, p-HOC₆H₄, C₆(CH₃)₅], ArSO₂SAr (Ar=C₆H₅, p-CH₃C₆H₄, p-ClC₆H₄), Ar₂SO₂ (Ar=p-CH₃C₆H₄, p-ClC₆H₄), ArSOAr' (Ar, Ar'=C₆H₅, p-CH₃C₆H₄; C₆H₅, o-CH₃C₆H₄; C₆H₅, p-ClC₆H₄; p-CH₃C₆H₄, o-CH₃C₆H₄), Ph₂Se, and PhSeSePh, were identified by comparison of their mass spectra with those on the available National Institute of Standards and Technology database. Their molar percentages (normalised) in the product were estimated by comparing the related GC peak areas on the basis of the assumption that the peak area is proportional to the number of moles of the related compound.

In order to support the above assumption, a standard sample containing Ph_2Se and PhSeSePh with the molar ratio of $Ph_2Se(mol)/PhSeSePh(mol)=2.0$ was made by dissolving known quantities of the diphenyl selenide (Ph_2Se) and diphenyl diselenide (PhSeSePh) reagents in CH_2Cl_2 . It was then measured by GC-MS, showing that ratio of the GC peak areas $Ph_2Se(peak)/PhSeSePh(peak)=2.2$. Thus, the relationship between the molar ratio and the ratio of peak areas is [Eqn (8)].

 $Ph_2Se(mol)/Ph_2SeSePh(mol)=0.91 \times [Ph_2Se(peak)/PhSeSePh(peak)]$ (8)

The molar ratio is approximately equal to the ratio of the corresponding GC peak areas with only about 10% difference.

CAUTION: Reactions should be conducted in a fume hood. Protective gloves should be worn because harmful gases such as hydrogen chloride and/or chlorine may be produced in various reactions detailed below.

Aluminium-chloride-($AlCl_3$)-catalysed reactions of thionyl chloride (SOCl.) with arenes PhX (X=CH, and Cl)

Approach 1: The reactions were conducted in the fume hood at 25 °C and 70 °C, respectively, with the molar ratio of PhX:SOCl₂:AlCl₃ being 2:1:1 and usage of SOCl₂ approximately 10 mmol. For each reaction, granular AlCl₃ was added piecewise to the PhX–SOCl₂ mixture (X=CH₃ or Cl) in a large test tube (~80 mL) as follows: First,

one piece of AlCl₃ was added and gas (HCl) bubbles started to form immediately. The piece of AlCl, was crushed using a stirring rod. When most of the piece of AlCl, had dissolved and bubbling occurred very slowly, another piece of AlCl₂ was added. All the AlCl₂ granules were eventually added into the PhX-SOCl, mixture piece-by-piece. The solution was initially light green and it turned dark green as the reaction went to completion, indicated by ceasing of bubbling after all the AlCl₃ had been added. Then iced water (40 mL) was poured into the reaction mixture and the green colour disappeared. This was followed by addition of diethyl ether (20 mL). All the contents were transferred into a separating funnel and shaken well to assure the organic product being fully extracted into the ether phase. The ether and water phases were separated. The water phase was extracted by diethyl ether (20 mL) again. Then all the ether solutions were combined and dried by anhydrous sodium sulfate. The dried ether solution was filtered off and left in the fume hood. Eventually, all the diethyl ether solvent evaporated, giving the final reaction product. The product was then characterised by GC-MS, and the results are shown in Table 1.

Approach 2: The reactions were conducted in the fume hood at 25 °C, with the molar ratio of PhX:SOCl₂:AlCl₃ being 2:1:1 and usage of SOCl₂ approximately 10 mmol. For each reaction, SOCl₂ was added dropwise to the PhX–AlCl₃ mixture (X=CH₃ or Cl) with constant stirring. The reaction took place quickly, indicated by bubbling as above. After all the SOCl₂ was added, the reaction went to completion, indicated by cessation of bubbling. Then aqueous work-up was performed as above. The final product was characterised by GC-MS, and the results are shown in Table 1.

The AlCl3-catalysed reaction of phenol (PhOH) with SOCl,

The reaction was conducted in the fume hood at 25 °C, with the molar ratio of PhOH:SOCl2:AlCl3 being 2:1:1 and the usage of SOCl2 approximately 10 mmol. A solution of PhOH in diethyl ether (10 mL) was poured all at once quickly into a SOCl,-AlCl, mixture in a large test tube. The resulting solution turned light brown immediately with a large amount of gas bubbles evolved. The gas produced from the reaction was tested by using wet KI-starch paper over the mouth of the test tube, and the paper turned dark blue $[Cl_3 + KI$ -starch $\rightarrow I_3$ starch (blue)+KCl], consistent with formation of Cl₂ in the reaction. After bubbling ceased (completion of the reaction), aqueous workup was performed as above. The GC-MS characterisation showed that the product contained 91% $(p-HOC_6H_4)_2S$ [bis(p-hydrophenyl) sulfide] and 9% p-ClC₆H₄OH (p-chlorophenol) (normalised yields in molar percentages). Another reaction was performed by adding AlCl₃ piecewise to a PhOH-SOCl, mixture, followed by aqueous work-up. The GC-MS characterisation showed that the product contained 51% (p-HOC₆H₄)₂S and 49% p-ClC₆H₄OH (normalised yields in molar percentages). $(p-HOC_6H_4)_3SO$ [bis(p-hydrophenyl) sulfoxide] was not identified from either of the reaction products. The results are included in Table 2.

Aluminium-chloride- $(AlCl_3)$ -catalysed reactions of thionyl chloride $(SOCl_2)$ with 1:1 mixtures of benzene (PhH) and substituted benzenes PhX (X=CH, and Cl)

The reactions were conducted in the fumehood at 25 °C, with the molar ratio of PhH:PhX:SOCl₂:AlCl₃ being 1:1:1:1 and usage of SOCl₂ approximately 10 mmol. For each reaction, granular AlCl₃ was added piecewise to the PhH–PhX–SOCl₂ mixture (X=CH₃ or Cl). The reaction was followed by aqueous work-up. The detailed procedure was the same as that for the above reactions in Approach 1. The product was characterised by GC-MS, and the results are shown in Table 3.

Producing S-aryl are nesulfonothioates $ArSO_2SAr$ (Ar=Ph, $p-CH_3C_6H_{ar}$ and, $p-CIC_6H_{ar}$) in significant yields

PhSO₂SPh: The yield enhancement was conducted by the AlCl₃catalysed reactions of benzene (PhH) and SOCl₂ in the fumehood at $0 \,^{\circ}C$ and $-10 \,^{\circ}C$, respectively, with the molar ratio of PhH:SOCl₂:AlCl₃ being 1:1:1 and usage of SOCl₂ approximately 25 mmol. For each of the reactions, with constant stirring PhH was added dropwise to a SOCl₂–AlCl₃ mixture in a large test tube. The solution turned green and gas bubbles were produced. After all the benzene had been added, the reaction mixture was kept at the same temperature (0 °C or -10 °C) for one hour. Then aqueous work-up was done, followed by extraction of the organic product using ether as above. The GC–MS analysis showed that the product made at each temperature contained three components, PhSO₂SPh, Ph₂S, and Ph₂SO, in different molar percentages (normalised) [Eqn (4)].

 $p-CH_3C_6H_4SO_2S(p-C_6H_4CH_3)$: The yield enhancement was conducted by the AlCl₃-catalysed reaction of toluene (PhCH₃) and SOCl₂ in the fumehood at -10 °C, with the molar ratio of PhCH₃:SOCl₂:AlCl₃ being 1:1:1 and usage of SOCl₂ approximately 25 mmol. With constant stirring PhCH₃ was added dropwise to a SOCl₂-AlCl₃ mixture. The procedure and observations were the same as those of the above benzene reactions. The GC-MS analysis showed that the product contained several components whose identities and molar percentages (normalised) are indicated in Eqn (5).

 $p-ClC_6H_4SO_2S(p-C_6H_4Cl)$: The yield enhancement was conducted by the AlCl₃-catalysed reactions of chlorobenzene (PhCl) and SOCl₂ in the fumehood at 0 °C, with the molar ratios of PhCl:SOCl₂:AlCl₃ being 1:1:1 and 1:2:2, respectively, and the usage of PhCl approximately 20 mmol. For both reactions, with constant stirring PhCl was added dropwise to the SOCl₂–AlCl₃ mixtures. The procedure and observations were the same as those of the above benzene and toluene reactions. The products were characterised by GC-MS. Three components, $p-ClC_6H_4SO_2S(p-C_6H_4Cl)$, $(p-ClC_6H_4)_2S$, and $(p-ClC_6H_4)_2SO$, were found in each of the products in different molar percentages (normalised) [Eqn (6)].

Aluminium-chloride- $(AlCl_y)$ - and iron(III)-chloride- $(FeCl_y)$ -catalysed reactions of selenyl chloride (SeOCl_) with benzene

The Lewis-acid-MCl₃-(M=Al and Fe)-catalysed reactions of benzene (PhH) with SeOCl, were performed in the fumehood at 25 °C, with the molar ratio of PhH:SeOCl₂:MCl₃ being 2:1:1 and usage of SeOCl₂ approximately 6 mmol. For the AlCl,-catalysed reaction, granular AlCl, was added piecewise to the PhH-SeOCl, mixture (slightly yellow) in a large test tube and then crushed. Initially, the mixture turned cloudy. Then it became brown with gas evolved. The gas was tested by using wet KI-starch paper over the mouth of the tube, and the paper turned dark blue [Cl₂+KI-starch \rightarrow I₂-starch (blue)+KCl], consistent with formation of Cl, in the reaction. When all the AlCl, was added and crushed, the liquid mixture became dark brown. The reaction mixture was maintained in the fumehood at 25 °C for 1 hour. Then aqueous work-up was conducted in the same manner as that adopted for the above SOCl, reactions as described in the Approach 1. Eventually, an orange liquid product was recovered from the ether extraction after the ether solvent evaporated. For the FeCl₃-catalysed reaction, powdery FeCl, was added in 10 aliquots to the PhH-SeOCl, mixture. The detailed procedure and observation were essentially the same as those for the AlCl₃-catalysed reaction. The MCl₃-(M=Cl and Fe)-catalysed reactions of SeOCl, with benzene were apparently much slower than the AlCl₂-catalysed reaction of SOCl₂ with benzene at the same temperature, which was indicated by much slower rate of bubbling in the SeOCl, reactions. The products from MCl₃-(M=Al and Fe)-catalysed reactions of benzene with SeOCl, were characterised by GC-MS, showing that two compounds, diphenyl selenide (Ph₂Se) and diphenyl diselenide (PhSeSePh), were produced in each reaction in different molar percentages [Eqn (7)], which were established by examining the GC peak areas according to Eqn (8). The initially expected diphenyl selenoxide (Ph,SeO) was not identified by GC-MS in either of the reaction products.

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