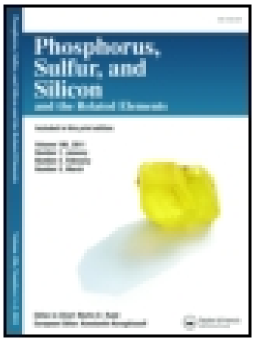

Phosphorus, Sulfur, and Silicon and the Related Elements

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# Iron(III) chloride ($FeCl_3$)-catalyzed electrophilic aromatic substitution of chlorobenzene with thionyl chloride ($SOCl_2$) and the accompanying auto-redox in sulfur to give diaryl sulfides ($Ar_2S$): Comparison to catalysis by aluminum chloride ($AlCl_3$)

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# Iron(III) chloride ($FeCl_3$)-catalyzed electrophilic aromatic substitution of chlorobenzene with thionyl chloride ($SOCl_2$) and the accompanying auto-redox in sulfur to give diaryl sulfides ($Ar_2S$): Comparison to catalysis by aluminum chloride ($AlCl_3$)

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**ABSTRACT**

The Lewis acids $MCl_3$ (M = Fe and Al)-catalyzed electrophilic aromatic (ArH) substitution reactions with thionyl chloride ($SOCl_2$) have been shown to give diaryl sulfoxide ($Ar_2SO$) and the reduced diaryl sulfide ($Ar_2S$). Under various selected conditions, the $FeCl_3$-catalyzed reactions of chlorobenzene gave substantially much higher percent yields of $Ar_2S$ (Ar = $p$-$ClC_6H_4$) than the reactions catalyzed by $AlCl_3$, showing that $FeCl_3$ facilitates the reduction in the sulfur center of $SOCl_2$. A $d_\pi \rightarrow p_\pi{}^*$ back bond between Fe(III) and the O=S group is thought to be responsible for enhancement of the reduction.

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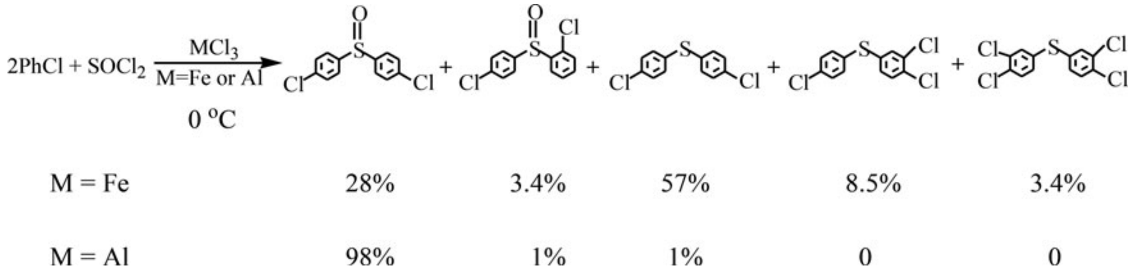
**KEYWORDS**
Iron catalysis; auto-redox, aromatic; CH substitution; chlorobenzene; $d_\pi$-$p_\pi{}^*$ bonding

**GRAPHICAL ABSTRACT**



## Introduction

Iron(III) chloride ($FeCl_3$) is a good Lewis acid and has been very widely and effectively employed as a catalyst in a variety types of organic chemical reactions.[1] Of these types of reactions, particularly interesting to us are the $FeCl_3$-catalyzed electrophilic aromatic substitution (EAS) reactions.[1,2] As part of the efforts made in this scenario, we have previously carried out the reaction of benzene with selenyl chloride ($SeOCl_2$) in the presence of $FeCl_3$ as a catalyst, and the reaction was found to give a mixture of diphenyl selenide ($Ph_2Se$) and diphenyl diselenide ($Ph_2Se_2$) without the formation of diphenyl selenoxide ($Ph_2SeO$).[3] We demonstrated that the formations of $Ph_2Se$ and $Ph_2Se_2$ occur via an EAS mechanism which is accompanied by auto-redox processes on the selenium center facilitated by $FeCl_3$ (Figure 1).[3] In this work, we extend the $FeCl_3$-catalyzed EAS reactions to thionyl chloride ($SOCl_2$), the sulfur analogue of $SeOCl_2$.

Previously, we have studied aluminum chloride ($AlCl_3$)-catalyzed EAS reactions of $SOCl_2$, and both diaryl sulfoxides ($Ar_2SO$, Ar=$C_6H_5$, $p$-$CH_3C_6H_4$, $o$-$CH_3C_6H_4$, and $p$-$ClC_6H_4$) and diaryl sulfides ($Ar_2S$, Ar=$C_6H_5$, $p$-$CH_3C_6H_4$, $o$-$CH_3C_6H_4$, $p$-$ClC_6H_4$, and $p$-$HOC_6H_4$) were produced in different percent yields depending on reaction conditions without formation of diphenyl disulfide ($Ph_2S_2$) under any conditions.[3,4] The formations of $Ar_2SO$ and $Ar_2S$ were demonstrated[3,4] to take place via the EAS and auto-redox on sulfur which are analogous to those involved in the $FeCl_3$-catalyzed EAS of $SeOCl_2$ as shown in Figure 1. In the present work, we study the $FeCl_3$-catalyzed reactions of $SOCl_2$ with chlorobenzene (PhCl). We have found that at the same conditions (temperature and the manner of mixing starting materials) all the $FeCl_3$-catalyzed reactions gave substantially much higher percent yields of diaryl sulfide $Ar_2S$ (Ar = 4-$ClC_6H_4$) than the reactions catalyzed by $AlCl_3$, showing that $FeCl_3$ facilitates the auto-redox process on the sulfur center in the reactions of PhCl with $SOCl_2$. The findings are unique, and we believe it is worthy to report them in the present article.

As reported previously by different workers, diaryl sulfoxides and sulfides have many important applications in organic synthesis and biomedical aspects.[5–10] Our findings in the role of $FeCl_3$ in facilitating the auto-redox of sulfur are also significant and have contributed new aspects to the iron catalysis.

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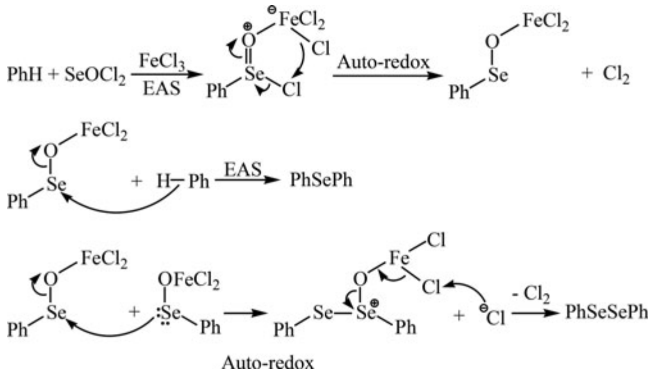


**Figure 1.** The FeCl$_3$-catalyzed reaction of benzene with SeOCl$_2$ giving Ph$_2$Se and Ph$_2$Se$_2$ via an EAS reaction and subsequent auto-redox processes on selenium.[3]

## Results and discussion

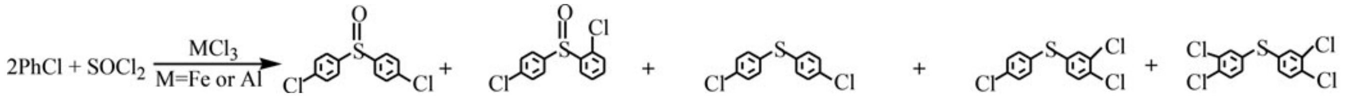
### *The FeCl$_3$-catalyzed reactions of PhCl with SOCl$_2$ and comparison to the AlCl$_3$ catalysis*

Table 1 shows the product distributions for the MCl$_3$ (M = Fe and Al)-catalyzed reactions of PhCl with SOCl$_2$ in different conditions (temperature, manner of mixing the starting materials, and molar ratio of the starting materials). At both 0°C and 25°C (Entries 1 and 2), the reactions catalyzed by FeCl$_3$ gave a total of five products; two isomers of diaryl sulfoxides and three reduced diaryl sulfides, with the total percentage (normalized) of the diaryl sulfides being about 69% and 57% at 0°C and 25°C, respectively. By contrast, the AlCl$_3$-catalyzed reactions at these temperatures mainly gave two sulfoxide isomers with only 1% and 7% (normalized) diaryl sulfide formed at 0°C and 25°C, respectively. When the temperature was further raised to 80°C (Entries 3 and 4), the FeCl$_3$-catalyzed reactions only gave the reduced diaryl sulfide products without formation of sulfoxide, while the AlCl$_3$-catalyzed reactions mainly gave two isomers of diaryl sulfoxide with only 6% diaryl sulfide formed. All these results demonstrate that by comparison to the AlCl$_3$ catalysis, utilization of FeCl$_3$ as a catalyst substantively facilitated the auto-redox process on sulfur so that the diaryl sulfides became the major products.

In addition to the auto-redox on sulfur to lead to the formation of (4-ClC$_6$H$_4$)$_2$S, the FeCl$_3$-catalyzed reactions of PhCl with SOCl$_2$ led to the formations of further chlorinated diaryl sulfide products (4-ClC$_6$H$_4$)S(3,4-Cl$_2$C$_6$H$_3$) and (3,4-Cl$_2$C$_6$H$_3$)$_2$S (Table 1). It is a remarkable feature observed for the reactions. At an elevated temperature (80°C) (Entries 3 and 4), formations of (4-ClC$_6$H$_4$)S(3,4-Cl$_2$C$_6$H$_3$) and (3,4-Cl$_2$C$_6$H$_3$)$_2$S became the major processes. When the molar ratio of PhCl : SOCl$_2$ : FeCl$_3$ = 2:1:1 (Entry 4), the molar percentages (normalized) of (4-ClC$_6$H$_4$)$_2$S, (4-ClC$_6$H$_4$)S(3,4-Cl$_2$C$_6$H$_3$), and (3,4-Cl$_2$C$_6$H$_3$)$_2$S in the product were 7%, 52%, and 41%, respectively. When the molar ratio of PhCl : SOCl$_2$ : FeCl$_3$ became 1:1:1, as the quantity of PhCl decreased and the quantity of SOCl$_2$ increased relatively, the percentage of (3,4-Cl$_2$C$_6$H$_3$)$_2$S in the product substantially increased coincident with the decrease in (4-ClC$_6$H$_4$)S(3,4-Cl$_2$C$_6$H$_3$), and the molar percentages (normalized) of (4-ClC$_6$H$_4$)$_2$S, (4-ClC$_6$H$_4$)S(3,4-Cl$_2$C$_6$H$_3$), and (3,4-Cl$_2$C$_6$H$_3$)$_2$S in the product became 3%, 24%, and 73%, respectively (Entry 3).

Our previous work has shown that the auto-redox on sulfur in the AlCl$_3$-catalyzed EAS reactions of SOCl$_2$ and the auto-redox on selenium in the AlCl$_3$- and FeCl$_3$-catalyzed EAS reactions of SeOCl$_2$ gave a byproduct of Cl$_2$.[3,4] Presumably and conceivably, the Cl$_2$ byproduct is also formed in the FeCl$_3$-catalyzed reaction of PhCl with SOCl$_2$. This is strongly evidenced by the observed chlorination of the aromatic rings (by Cl$_2$) to lead to the formations of (4-ClC$_6$H$_4$)S(3,4-Cl$_2$C$_6$H$_3$), and (3,4-Cl$_2$C$_6$H$_3$)$_2$S in all the FeCl$_3$-catalyzed reactions (Table 1). Comparing to the previously studied AlCl$_3$-catalyzed reactions,[3,4] the production of Cl$_2$ in the FeCl$_3$-catalyzed reactions, along with the conversion of S(IV) in SOCl$_2$ to S(II) in Ar$_2$S, supports a similar, proposed auto-redox mechanism as

**Table 1.** Distributions of products formed in the MCl$_3$ (M = Fe and Al)-catalyzed reactions of PhCl with SOCl$_2$[a]

|  | | | | | |
|---|---|---|---|---|---|
| M = Fe | 28% | 3.4% | 57% | 8.5% | 3.4% |
| M = Al[b] | 98% | 1% | 1% | 0 | 0 |
| **(Entry 1)** | SOCl$_2$ added dropwise to the PhCl/MCl$_3$ mixture at **0°C** PhCl : SOCl$_2$ : MCl$_3$ = 1:1:1 (molar ratio) | | | | |
| M = Fe | 39% | 4% | 38% | 7% | 12% |
| M = Al | 76% | 17% | 7% | 0 | 0 |
| **(Entry 2)** | MCl$_3$ added to the PhCl/SOCl$_2$ mixture at **25°C** PhCl : SOCl$_2$ : MCl$_3$ = 1:1:1 (molar ratio) | | | | |
| M = Fe | 0 | 0 | 3% | 24% | 73% |
| M = Al[c] | 78% | 16% | 6% | 0 | 0 |
| **(Entry 3)** | SOCl$_2$ added dropwise to the PhCl/MCl$_3$ mixture at **80°C** PhCl : SOCl$_2$ : MCl$_3$ = 1:1:1 (molar ratio) | | | | |
| M = Fe | 0 | 0 | 7% | 52% | 41% |
| M = Al | 79% | 21% | 0 | 0 | 0 |
| **(Entry 4)** | SOCl$_2$ added dropwise to the PhCl/MCl$_3$ mixture at **80°C** PhCl : SOCl$_2$ : MCl$_3$ = 2:1:1 (molar ratio) | | | | |

[a] All the percentages are relative normalized yields (GC yields), determined by comparison of areas of the GC spectra of related components on the basis, as previously established,[3] that the peak area is proportional to the number of moles of the component.

[b] Essentially, only the *para*-isomer of diaryl sulfoxide was formed based on GC-MS analysis. The overall isolated percent yield was determined to be 63% by comparison of the actually recovered mass of the product with the theoretical yield of diaryl sulfoxide. Therefore, the absolute conversion yield of the *para*-isomer should be 62% (98% × 63%).

[c] Mainly, the *para*- and *ortho*-isomers of diaryl sulfoxide were formed with overall isolated percent yield being 80%. Therefore, the absolute conversion yields of the *para*-isomer and *ortho*-isomer should be 62% (78% × 80%) and 13% (16% × 80%), respectively.

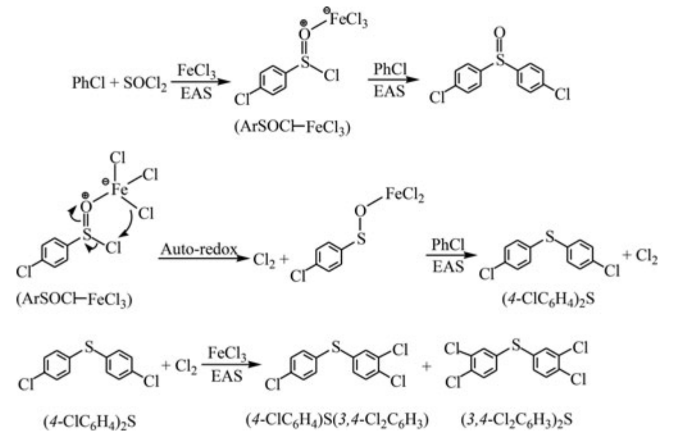


**Figure 2.** Mechanism for the $FeCl_3$-catalyzed reaction of PhCl with $SOCl_2$.

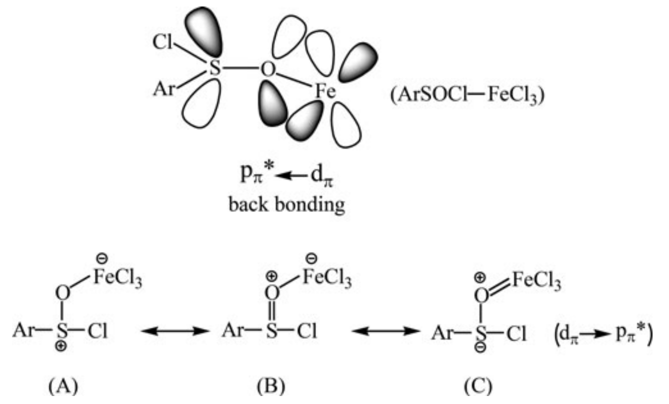


**Figure 3.** The $d_\pi$–$p_\pi*$ back bonding between Fe(III) and S=O in the ArSOCl–$FeCl_3$ adduct molecule and possible resonance structures of ArSOCl–$FeCl_3$. The $d_\pi$ ($d_{yz}$) orbital is perpendicular to the $FeCl_3$ molecule plane (the *xy*-plane).

shown in Figure 2.[11] The overall process is demonstrated in Figure 2.

Previously, we have identified chlorination of PhOH to form minor $p$-$ClC_6H_4OH$ in the course of an $AlCl_3$-catalyzed reaction of phenol (PhOH) with $SOCl_2$ giving ($p$-$HOC_6H_4)_2S$ and the $Cl_2$ by-product as a result of the auto-redox on sulfur.[3] By comparison of the reaction with the molar ratio of PhCl : $SOCl_2$ : $FeCl_3$ = 2:1:1 (Entry 4) and the reaction with the molar ratio of PhCl : $SOCl_2$ : $FeCl_3$ = 1:1:1 (Entry 3) at 80°C (Table 1), as the relative quantity of $SOCl_2$ increased and became excess and the relative quantity of PhCl decreased and became deficit, the extent of chlorination on the aromatic rings of the initially formed $(4\text{-}ClC_6H_4)_2S$ was enhanced. As a result, the 1:1:1 reaction (Entry 3) gave much higher percentage (73%) of $(3,4\text{-}Cl_2C_6H_3)_2S$ than that (41%) of $(3,4\text{-}Cl_2C_6H_3)_2S$ produced in the 2:1:1 reaction (Entry 4). As the percentage of $(3,4\text{-}Cl_2C_6H_3)_2S$ was getting higher, the percentage of $(4\text{-}ClC_6H_4)S(3,4\text{-}Cl_2C_6H_3)$ in the product was getting correspondingly lower.

## *The iron(III) d-orbital facilitated intramolecular auto-redox processes on sulfur in the $FeCl_3$-catalyzed EAS reactions of $SOCl_2$*

The studies of $MCl_3$ (M = Fe and Al)-catalyzed reactions of PhCl with $SOCl_2$ have shown that under the same conditions, the $FeCl_3$-catalyzed reactions always produce much higher percent yields of diaryl sulfides than the reactions catalyzed by $AlCl_3$. Under certain conditions (Table 1 Entries 3 and 4, reactions at 80°C), all the products generated from the $FeCl_3$-catalyzed reactions are diaryl sulfides without formation of diaryl sulfoxides, while the $AlCl_3$ catalyzed reactions, on the other hand, give diaryl sulfoxides as major products. This shows that the utilization of $FeCl_3$ as a catalyst for the EAS reactions of $SOCl_2$ greatly facilitates the intramolecular auto-redox on sulfur (Figure 2) to lead to formation of diaryl sulfides. We believe that this effect is accomplished via the iron(III) d-orbital participation in the overall reactions.

The symmetry of the empty $p_\pi*$ orbital (the antibonding $\pi*$ orbital) in the S=O bond domain of the ArSOCl-$FeCl_3$ intermediate (Figure 2) matches the symmetry of the filled $d_\pi$ orbital in the iron atom. Therefore, the $d_\pi$ and $p_\pi*$ orbitals can overlap effectively in sideways to form a $d_\pi$ –> $p_\pi*$ back bond between the iron and oxygen atoms in ArSOCl-$FeCl_3$ (Figure 3). As a result, the $d_\pi$ electrons in iron flow into the S=O $p_\pi*$ orbital to partially neutralize the positive charge in sulfur decreasing its electrophilicity. The resonance structure (C) in Figure 3 results from the $d_\pi$ –> $p_\pi*$ back bonding and further demonstrates the electron transfer from iron to sulfur. Consequently, the sulfur center in ArSOCl-$FeCl_3$ cannot be attacked efficiently by the nucleophilic aromatic ring in PhCl to make $Ar_2SO$ (Ar = $p$-$ClC_6H_4$). Instead, the intramolecular auto-redox process in ArSOCl-$FeCl_3$, as shown in Figure 2, becomes more prominent, much faster than the EAS of ArH with ArSOCl-$FeCl_3$, to give $Ar_2S$ as the major or sole product and the $Cl_2$ by-product. We believe that this accounts for the role of $FeCl_3$ in facilitating the auto-redox processes in the $FeCl_3$-catalyzed EAS reactions of $SOCl_2$. Recently, we have found that by comparison with the $AlCl_3$ catalysis, the $FeCl_3$-catalyzed reaction of benzene with $SeOCl_2$, the selenium analogue of $SOCl_2$, generated higher yield of the reduced $Ph_2Se_2$ indicating a similar role of $FeCl_3$ in facilitating the analogous auto-redox on selenium in the EAS reactions of $SeOCl_2$.[3]

## Conclusions

In this work, the previously established $FeCl_3$-catalyzed EAS reaction of $SeOCl_2$ [3] has been extended to $SOCl_2$ (the sulfur analogue) and the results are compared to the catalysis by $AlCl_3$. Under the same conditions, including reaction temperature, the molar ratio of the reactants, and the manner of mixing starting materials, the $FeCl_3$-catalyzed reactions of PhCl with $SOCl_2$ have been found to give substantially much higher percent yields of diaryl sulfides $Ar_2S$ (Ar = $4$-$ClC_6H_4$) than the reactions catalyzed by $AlCl_3$, showing that $FeCl_3$ facilitates the auto-redox in the sulfur center of $SOCl_2$. A $d_\pi$ –> $p_\pi*$ back bond between the iron and oxygen atoms in the ArSOCl-$FeCl_3$ intermediate formed in the first step of EAS reaction is proposed to account for the enhancement of the auto-redox by $FeCl_3$. The $d_\pi$ electrons in iron can be transferred into the empty S=O $p_\pi*$ orbital to decrease the electrophilicity in sulfur. As a result, the sulfur center in ArSOCl-$FeCl_3$ becomes much less reactive towards an aromatic ring. Instead, the intramolecular auto-redox in ArSOCl-$FeCl_3$

takes place predominately to give $Ar_2S$ as the major or a sole product.

Iron catalysis has been shown to play very important roles in organic chemistry.[1,2] We believe that our present research has made contributions of new and interesting aspects to this significant area.

## Experimental

### Chemical reagents

Thionyl chloride ($SOCl_2$) (purified) from J. T. Baker Chemical Company was used. Chlorobenzene (PhCl) (99%) were obtained from Sigma Aldrich. Granular anhydrous aluminum chloride ($AlCl_3$) (99%, extra pure) was obtained from Acros Organics. Powdery iron(III) chloride ($FeCl_3$) (98%), diethyl ether (solvent), dichloromethane (99.9%, the solvent for GC-MS samples), and anhydrous sodium sulfate (99.5%, drying agent) 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 in an approximate 1% (m/m) dilution in dichloromethane. One-microliter of the solution was injected onto a Chrompack CP-SIL 8-CB 30 m × 0.25 mm capillary column using a He carrier gas of 1.0 mL/min, a 1/100 injection split ratio, and a temperature ramp of 150°C to 240°C (10°C/min). All chemical compounds were eluted in 10 min. The individual compounds contained in each product, including $Ar_2SO$ ($Ar = p\text{-}ClC_6H_4$), ArSOAr′ (Ar, $Ar' = p\text{-}ClC_6H_4$, $o\text{-}ClC_6H_4$), $Ar_2S$ ($Ar = 4\text{-}ClC_6H_4$, and $3,4\text{-}Cl_2C_6H_3$), and ArSOAr′ (Ar, $Ar' = 4\text{-}ClC_6H_4$, $3,4\text{-}Cl_2C_6H_3$), were identified by comparison of their mass spectra with those on the available NIST database. Their molar percentages (normalized) in the product were estimated, as previously established,[3] by comparing the related GC peak areas on such a basis that the peak area is proportional to the number of moles of the related compound.

### The $MCl_3$ (M = Fe and Al)-catalyzed reactions of PhCl with $SOCl_2$

**Approach 1**: The reactions were conducted in the fumehood at 0°C with the molar ratio of PhCl : $SOCl_2$ : $MCl_3$ being 1:1:1 and usage of $SOCl_2$ approximately 10 mmol [PhCl (1.13 g, 10.0 mmol), $SOCl_2$ (1.19 g, 10.0 mmol), and $AlCl_3$ (1.33 g, 10.0 mmol) or $FeCl_3$ (1.62 g, 10.0 mmol)]. For each reaction, $SOCl_2$ was added dropwise to the PhCl–$MCl_3$ (M = Fe or Al) mixture in a large test tube (80 mL) with constant stirring (For the $AlCl_3$-catalyzed reaction, $SOCl_2$ was added after the granular $AlCl_3$ had been mostly crushed). The reaction took place quickly, indicated by bubbling (formation of HCl) as above. After all the $SOCl_2$ was added, the reaction went to completion (in about 2 h), indicated by the cessation of bubbling. Then iced water (40 mL) was poured into the reaction mixture. This was followed by the addition of diethyl ether (20 mL). All the contents were transferred into a separatory funnel and shaken well to ensure that the organic product had been 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 fumehood. Eventually, all the diethyl ether solvent evaporated, giving the final reaction product. The product was then characterized by GC-MS, and the results are shown in Table 1 (Entry 1).

**Approach 2**: The reactions were conducted in the fumehood at 25°C with the molar ratio of PhCl : $SOCl_2$ : $MCl_3$ being 1:1:1 and usage of $SOCl_2$ approximately 10 mmol (as above). For the $FeCl_3$-catalyzed reactions, powdery $FeCl_3$ was added in 10 aliquots to the PhCl–$SOCl_2$ mixture in a large test tube (80 mL). The reaction took place quickly, indicated by bubbling as above. After all the $FeCl_3$ was added, the reaction went to completion, indicated by the cessation of bubbling. Then the aqueous work-up was performed as above. The final product was characterized by GC-MS, and the results are shown in Table 1 (Entry 2). For the $AlCl_3$-catalyzed reactions, granular $AlCl_3$ was added piecewise to the PhCl–$SOCl_2$ mixture in a large test tube (80 mL) as follows: First, one piece of $AlCl_3$ was added and gas (HCl) bubbles started to form immediately. The piece of $AlCl_3$ was crushed using a stirring rod. When most of the pieces of $AlCl_3$ had dissolved and bubbling occurred very slowly, another piece of $AlCl_3$ was added. All the $AlCl_3$ granules were eventually added into the PhCl–$SOCl_2$ mixture piece-by-piece. The reaction went to completion, indicated by the cessation of bubbling after all the $AlCl_3$ had been added. Then an aqueous work-up was performed as above. The final product was characterized by GC-MS, and the results are shown in Table 1 (Entry 2).

**Approach 3**: The reactions were conducted in the fumehood at 80°C with the molar ratio of PhCl : $SOCl_2$ : $MCl_3$ being 1:1:1 and usage of $SOCl_2$ approximately 10 mmol (as above). For each reaction, $SOCl_2$ was added dropwise to the PhCl–$MCl_3$ (M = Fe or Al) mixture in a large test tube with constant stirring (For the $AlCl_3$-catalyzed reaction, $SOCl_2$ was added after the granular $AlCl_3$ had been mostly crushed). The procedure and observations were the same as those for the above reactions conducted at 0°C. The final product was characterized by GC-MS, and the results are shown in Table 1 (Entry 3).

**Approach 4**: The reactions were conducted in the fumehood at 80°C with the molar ratio of PhCl : $SOCl_2$ : $MCl_3$ being 2:1:1 and usage of $SOCl_2$ approximately 10 mmol [PhCl (2.26 g, 20.1 mmol), $SOCl_2$ (1.19 g, 10.0 mmol), and $AlCl_3$ (1.33 g, 10.0 mmol) or $FeCl_3$ (1.62 g, 10.0 mmol)]. For each reaction, $SOCl_2$ was added dropwise to the PhCl–$MCl_3$ (M = Fe or Al) mixture in a large test tube with constant stirring (For the $AlCl_3$-catalyzed reaction, $SOCl_2$ was added after the granular $AlCl_3$ had been mostly crushed). The procedure and observations were the same as those for the above 1:1:1 reactions at 80°C (Approach 3). The final product was characterized by GC-MS, and the results are shown in Table 1 (Entry 4).

## Funding

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11. Due to lack of the light (photochemical conditions) and no available radical initiators, the reaction cannot follow a radical mechanism.