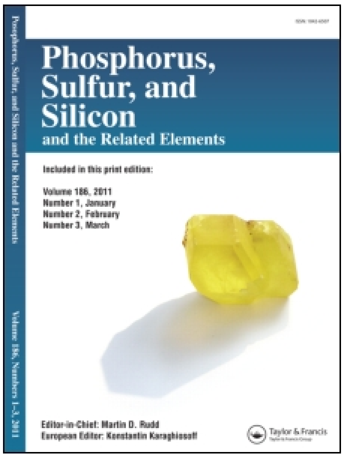

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Formation of Diphenyl Sulfoxide and Diphenyl Sulfide via the Aluminum Chloride-Facilitated Electrophilic Aromatic Substitution of Benzene with Thionyl Chloride, and a Novel Reduction of Sulfur (IV) to Sulfur (II)

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FORMATION OF DIPHENYL SULFOXIDE AND DIPHENYL SULFIDE VIA THE ALUMINUM CHLORIDE–FACILITATED ELECTROPHILIC AROMATIC SUBSTITUTION OF BENZENE WITH THIONYL CHLORIDE, AND A NOVEL REDUCTION OF SULFUR (IV) TO SULFUR (II)

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The aluminum chloride ($AlCl_3$)–facilitated electrophilic aromatic substitution (EAS) reaction of benzene (PhH) with thionyl chloride ($SOCl_2$) in the molar ratio of PhH:$SOCl_2$:$AlCl_3$ = 2:1:1 was studied under different conditions. At about 70°C, adding granular $AlCl_3$ (equimolar to $SOCl_2$) piecewise to a 2:1 mixture of PhH and $SOCl_2$ led to formation of a highly pure (99.9%) sole product of diphenyl sulfoxide (Ph_2SO) in an isolated yield of 85% after aqueous workup. It represents a simple and very efficient synthesis of Ph_2SO, an important fundamental organic reagent. At about 0°C, adding PhH (twice the molar quantity of $SOCl_2$) to a 1:1 mixture of $SOCl_2$ and $AlCl_3$ gave both diphenyl sulfide Ph_2S (yield: 37%) and Ph_2SO (yield: 27%) after aqueous workup, together with a small amount of S-phenyl benzenesulfonothioate $PhSO_2SPh$ (yield: about 5%) and a trace amount of diphenyl sulfone (Ph_2SO_2). A possible mechanism has been proposed to account for formation of all these products, especially for the formation of Ph_2S [S (II)] from $SOCl_2$ [S (IV)], which involves a novel reduction of sulfur in the course of the EAS reaction.

Keywords Diphenyl sulfide; diphenyl sulfoxide; EAS; reduction; sulfur; thionyl chloride

INTRODUCTION

Diphenyl sulfoxide (Ph_2SO) and diphenyl sulfide (Ph_2S) are important reagents in organic synthesis.[1,2] Ph_2S is commonly synthesized by the reaction of benzene (PhH) with disulfur dichloride (S_2Cl_2) in the presence of anhydrous aluminum chloride ($AlCl_3$).[3] It gives a good yield, but the method is complex and tedious. Ph_2SO, on the other hand, is usually made by catalytic oxidation of Ph_2S.[4,5] The preparation often suffers with overoxidation to the diphenyl sulfone (Ph_2SO_2) side product. In order to overcome this difficulty, a different method was developed by the reaction of Ph_2S with sulfuryl chloride (SO_2Cl_2), which gives moderate yield of Ph_2SO after crystallization.[6] In this article, we report a simple synthesis of Ph_2SO by the $AlCl_3$-catalyzed Friedel–Crafts reaction of PhH with thionyl chloride ($SOCl_2$). Upon mild heating (70°C) and by optimizing the manner of mixing

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the starting materials, this reaction (after aqueous workup) has led to efficient formation of highly pure Ph_2SO (99.9%) as a sole product in an isolated yield of 85%. Olah and Nishimura[7] have studied the $AlCl_3$-catalyzed electrophilic aromatic substitution (EAS) reactions of benzene and toluene with arenesulfonyl chlorides (ArSOCl), which is analogous to $SOCl_2$. The reactions gave various aryl sulfoxides at 25°C. However, no study of the $AlCl_3$-catalyzed EAS reactions of arenes including benzene and toluene with $SOCl_2$ had been reported prior to our current work. Among other things, to our surprise, when the reaction was performed at 0°C and the manner of mixing the starting materials was altered, Ph_2S was formed as a major product in a significant yield. Clearly, formation of Ph_2S [S (II)] in the reaction of PhH with $SOCl_2$ [S (IV)] in the presence of $AlCl_3$ was accompanied by reduction of sulfur, which is the electrophilic center for the EAS reaction. Such an aromatic C–H bond functionalization is unprecedented. The current study of reaction of benzene with thionyl chloride aided by aluminum chloride is of significance in both organic synthesis and mechanisms.

RESULTS AND DISCUSSION

Benzene has been shown to undergo general extensive EAS reactions with chlorine, alkyl chlorides, and acyl chlorides in the presence of $AlCl_3$ giving chlorobenzene, alkylbenzenes, and aromatic ketones, respectively.[8,9] Similar to the above EAS reactions, especially analogous to the reactions of acyl chlorides (RCOCl), $SOCl_2$ was initially expected to undergo double consecutive EAS (Fiedel–Crafts) reactions with PhH in the presence of $AlCl_3$ as a catalyst to give Ph_2SO as shown below when the starting materials were mixed in the molar ratio of PhH:$SOCl_2$:$AlCl_3$ = 2:1:1.

$$2PhH + SOCl_2 \xrightarrow{AlCl_3} Ph_2SO + 2HCl \qquad \text{(Rxn1)}$$

However, only under carefully selected and controlled conditions did this reaction give a sole product Ph_2SO as shown in Rxn. (1). In many other cases, depending on the temperature and the manner in which the starting materials were actually mixed, this reaction was shown (Table I) to usually give several products, including Ph_2SO, Ph_2S, S-phenyl benzenesulfonothioate ($PhSO_2SPh$), and Ph_2SO_2, in various yields. A possible mechanism has been proposed to account for formation of all these products (Figure 1).

Formation of Ph_2SO via Approach (A)

When granular $AlCl_3$ (equimolar to $SOCl_2$) was added in aliquots (piecewise) to a 2:1 (molar ratio) mixture of PhH and $SOCl_2$ at about 70°C, the reaction gave a highly pure (99.9%) sole product of Ph_2SO [Rxn. (1)] in an isolated yield of 85% after aqueous workup. The high yield and outstanding purity of the Ph_2SO product indicated that the reaction followed the double consecutive EAS mechanism under the applied conditions. First, as established previously,[10,11] $SOCl_2$ and $AlCl_3$ combined to form a Cl_2SO-$AlCl_3$ zwitterionic adduct via an O→Al coordination bond (Figure 1). After the Cl_2SO-$AlCl_3$ adduct completed an EAS reaction with the first benzene molecule, the intermediate product (PhSOCl-$AlCl_3$) was immediately attacked by a second benzene molecule (Approach A), exclusively effecting another EAS reaction to give Ph_2SO. The postulated approaches (B) and (C) did not occur. When $SOCl_2$ (equimolar to $AlCl_3$) was added in aliquots (dropwise) to a 2:1 (molar ratio) mixture of PhH and $AlCl_3$ at about 25°C, the reaction also gave a pure

Table I Product distribution (after aqueous workup) for reaction of benzene (PhH) and thionyl chloride ($SOCl_2$) in the presence of aluminum chloride ($AlCl_3$) with the molar ratio of PhH:$SOCl_2$:$AlCl_3$ = 2:1:1 under different conditions

Temp (°C)	Manner of mixing	Ph_2SO (yield)	Ph_2S (yield)	Ph_2SO_2SPh (yield)	Ph_2SO_2 (yield)
70	$AlCl_3$ added piecewise to the PhH-$SOCl_2$ mixture	85% (isolated)	0%	0%	0%
25	$AlCl_3$ added piecewise to the PhH-$SOCl_2$ mixture	75% (GC)	3% (GC)	5% (GC)	Trace amount
25	$SOCl_2$ added dropwise to the PhH-$AlCl_3$ mixture	78% (isolated)	0%	0%	0%
25	PhH poured at once into the $SOCl_2$-$AlCl_3$ mixture	52% (GC)	22% (GC)	5% (GC)	Trace amount
0	$AlCl_3$ added piecewise to the PhH-$SOCl_2$ mixture	75% (GC)	5% (GC)	5% (GC)	Trace amount
0	$SOCl_2$ added dropwise to the PhH-$AlCl_3$ mixture	72% (GC)	6% (GC)	5% (GC)	Trace amount
0	PhH poured at once into the $SOCl_2$-$AlCl_3$ mixture	27% (GC)	37% (GC)	5% (GC)	Trace amount

(99%) sole product of Ph_2SO [Rxn. (1)] in an isolated yield of 78% after aqueous workup. The results again indicated almost exclusive double consecutive EAS reactions of benzene with the Cl_2SO-$AlCl_3$ adduct via approach (A). Approaches (B) and (C) essentially did not take place. In each of these cases, because $AlCl_3$ or $SOCl_2$ was added in aliquots, the Cl_2SO-$AlCl_3$ adduct was in deficit relative to the quantity of benzene during the overall reaction. As a result, the first EAS product (PhSOCl-$AlCl_3$) remained at low concentration. Therefore, the postulated intramolecular (unimolecular) and intermolecular (bimolecular) auto-redox processes (B and C, respectively) would reasonably be thought to be too slow to actually take place. Instead, after PhSOCl-$AlCl_3$ was produced from the first EAS reaction, it was immediately attacked by the excessive benzene (Approach A) exclusively to give Ph_2SO as a sole product.

Traditionally, Ph_2SO has been made by catalytic oxidation of Ph_2S.[4,5] Ph_2S is commonly prepared by reaction of benzene with S_2Cl_2 in the presence of $AlCl_3$.[3] In this work, a more direct, simpler, and perhaps more efficient route to the synthesis of a high yield of Ph_2SO has been developed via the EAS reaction of benzene with $SOCl_2$ catalyzed by $AlCl_3$. Because of the simplicity of the reaction mechanism, side reactions only took place to a very minimal extent (indicated by the green color but removed readily by aqueous workup), and high purity of Ph_2SO has been produced without any further purification process.

At lower temperatures such as 25°C and 0°C (Table I), when $AlCl_3$ was added piecewise to a PhH:$SOCl_2$ = 2:1 mixture, the reactions gave small amounts of Ph_2S (yield: 3–5%], $PhSO_2SPh$ (yield: about 5%), and Ph_2SO_2 (trace amount) in addition to the major product Ph_2SO (yield: about 75%). When $SOCl_2$ was added dropwise to a PhH:$AlCl_3$ = 1:1 mixture at 0°C, essentially, the same situation was found. All this indicated (Figure 1) that higher temperatures favor approach (A), leading to formation of Ph_2SO, while lower temperatures favor approaches (B) and (C), leading to formation of Ph_2S and $PhSO_2SPh$.

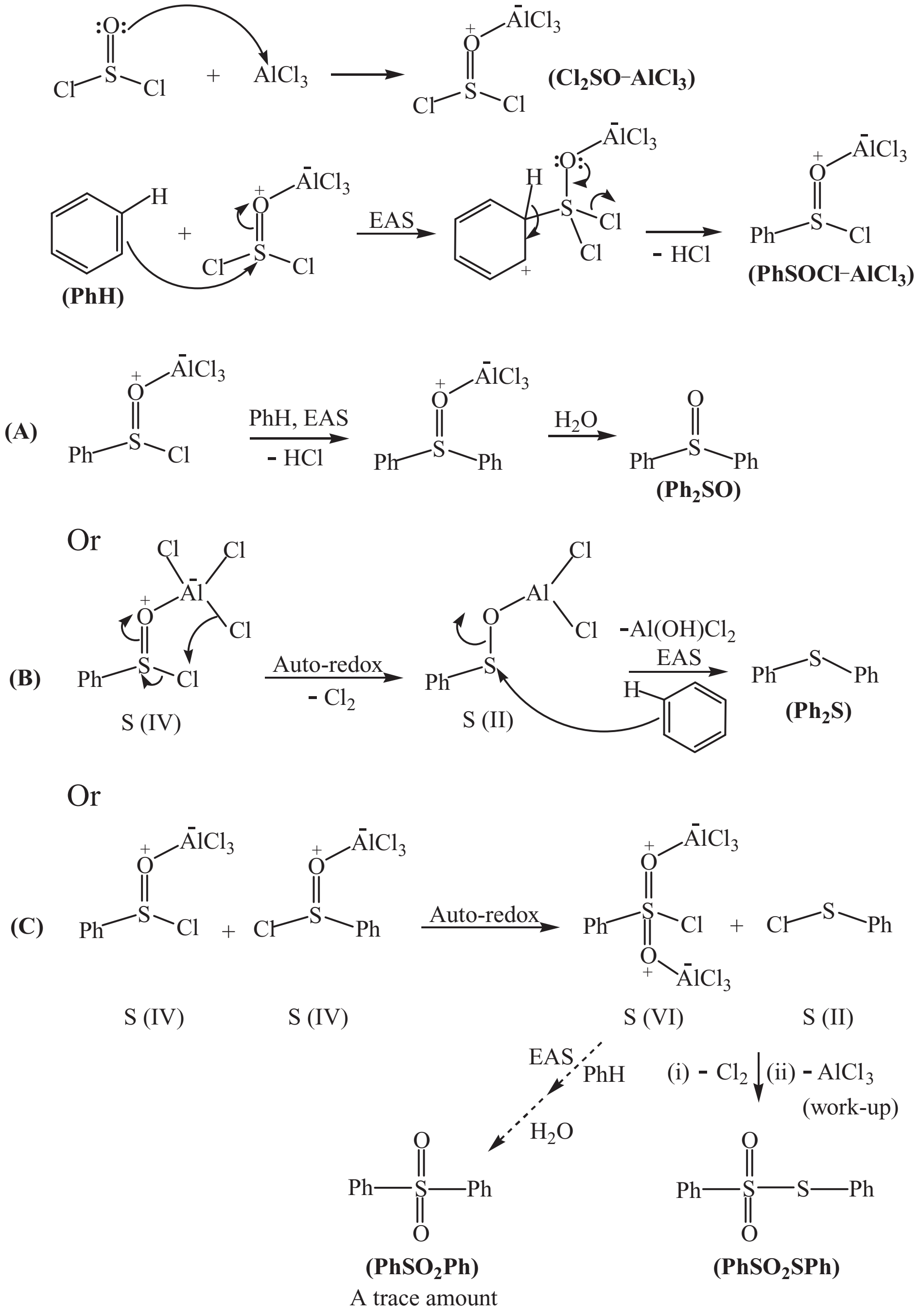

Figure 1 Proposed mechanism for the aluminum chloride ($AlCl_3$)–facilitated electrophilic aromatic substitution of benzene (PhH) with thionyl chloride ($SOCl_2$), possibly giving several products.

Formation of Ph_2S via a Possible Auto-Redox Process (Approach B)

Since under certain conditions and at relatively low temperatures reaction of PhH with $SOCl_2$ in a 2:1 molar ratio in the presence of $AlCl_3$ led to formation of Ph_2S in various yields in addition to Ph_2SO (Table I), attempted preparation of Ph_2S by a simple EAS reaction of benzene with $SOCl_2$ by the aid of $AlCl_3$ was performed at about 0°C. Having found that maintaining the Cl_2SO-$AlCl_3$ adduct (Figure 1) in deficit relative to the quantity of benzene facilitates approach (A) (formation of Ph_2SO), but disfavors approach (B) (formation of Ph_2S), an opposite manner of mixing the starting materials was employed. PhH (twice the molar quantity of $SOCl_2$) was poured all at once into a 1:1 (molar ratio) mixture of $SOCl_2$ and $AlCl_3$ at about 0°C. The reaction led to formation of both Ph_2S (yield: 37%) and Ph_2SO (yield: 27%) after an aqueous workup. In addition, a minor amount of $PhSO_2SPh$ (yield: about 5%) and a trace amount of Ph_2SO_2 were formed.

$$2PhH + SOCl_2 + AlCl_3 \xrightarrow{0^\circ C} \xrightarrow{H_2O} \underset{37\%}{Ph_2S} + \underset{27\%}{Ph_2SO} + \underset{\text{about }5\%}{PhSO_2SPh} + \underset{\text{trace amount}}{PhSO_2Ph} \quad \text{(Rxn2)}$$

It is interesting to notice that formation of Ph_2S containing S (II), a major product of Rxn. (2) in a significant yield, from $SOCl_2$ containing S (IV) involved a reduction process in the sulfur atom, while no reducing agent was added to the reaction system. We believe that the first EAS product ($PhSOCl$-$AlCl_3$), after being formed, might undergo a major fast intramolecular auto-redox reaction (approach B) eventually giving Ph_2S (Figure 1) in addition to forming Ph_2SO via approach (A). An Al–Cl bond in $PhSOCl$-$AlCl_3$ (the first EAS product) can reasonably be a chloride (Cl^-) donor (nucleophilic). The S–Cl chlorine atom is apparently activated by the electronegative sulfoxide (S=O) group, possibly being electrophilic and readily attacked by the Al–Cl chloride to give Cl_2. Formation of Cl_2 in the reaction was experimentally identified.[12] S (IV) was in turn reduced to S (II). In this reaction, because benzene was added all at once to a 1:1 $SOCl_2$–$AlCl_3$ mixture, the concentration of $PhSOCl$-$AlCl_3$ was relatively high. Approach (B) could possibly take place rapidly as a major process to give Ph_2S. In this process, high affinity of aluminum to oxygen was believed to aid cleavage of the S–O bond (removal of oxygen from sulfur), facilitating a second EAS reaction. Concurrently, approach (A) also took place to a substantial extent giving Ph_2SO.

When the reaction was performed at 25°C in the same manner, the product distribution (52% Ph_2SO, 22% Ph_2S, and 5% $PhSO_2SPh$) indicates (Figure 1) a substantial increase in the ratio of Ph_2SO:Ph_2S relative to that at 0°C (37% Ph_2SO and 27% Ph_2S). The results demonstrate that at 25°C, approach (A) became the major process and approaches (B) and (C) were minor processes.

A postulated minor intermolecular auto-redox (oxygen exchange) process between two $PhSOCl$-$AlCl_3$ molecules (approach C) has been proposed (Figure 1) to account for the formation of a small amount of $PhSO_2SPh$ and a trace amount of Ph_2SO_2. The postulated S (VI) species was believed to be reasonably responsible for the formation of Ph_2SO_2 via an EAS reaction with benzene. p-Toluenesulfonyl chloride [analogous to the S (VI) species] has been previously shown to undergo aluminum chloride–catalyzed EAS reactions with benzene and toluene giving sulfone (analogous to Ph_2SO_2) products.[13] On the other hand, identification of Ph_2SO_2 as a reaction product supported formation of the S (VI) species in the course of the reaction. The combination of the S (VI) and S (II) species (sulfonothioesterification) might possibly be responsible for formation of $PhSO_2SPh$.

EXPERIMENTAL

Chemical Reagents

Thionyl chloride ($SOCl_2$) (purified) from J.T. Baker Chemical Company was used. Benzene (PhH) (99.9%) was obtained from Sigma Aldrich. Granular anhydrous aluminum chloride ($AlCl_3$) (99%, extra pure) and both the authentic diphenyl sulfoxide (Ph_2SO) (98%) and diphenyl sulfide (Ph_2S) (99%) reagents (GC-MS standards) were obtained from Acros Organics. Anhydrous sodium sulfate (99.5%, drying agent) and dichloromethane (99.9%, the solvent for GC-MS samples) were both purchased from Fisher Scientific Company.

The GC-MS Measurements

Reaction products were identified and quantified using a Varian CP-3800 gas chromatograph–Varian Saturn 2200 mass spectrometer. Reaction products and samples of Ph_2S and Ph_2SO reagents were prepared in an approximate 1% (m/m) dilution in dichloromethane. One μL of this 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. For individual samples of the authentic Ph_2S and Ph_2SO reagents, a single major peak (over 99%) was identified for each with only a few very low peaks found less than 1%, indicating the purity of each of the authentic reagents and thermal stability for Ph_2S and Ph_2SO at the analysis temperature. The mass spectra of Ph_2S and Ph_2SO were consistent with fragmentation patterns available from a NIST database on the instrument. The retention times and mass spectra of Ph_2S and Ph_2SO identified by GC-MS in the samples of various reaction products were found to be consistent with those of the authentic Ph_2S and Ph_2SO reagents measured under the same conditions. In the samples of reaction products, which contained both Ph_2S and Ph_2SO, their percentages were determined by comparing the related GC peak areas with those of a sample made up with known contents of Ph_2S and Ph_2SO using the authentic reagents. In some experiments, small amounts of diphenylsulfone (Ph_2SO_2) and S-phenyl benzenesulfonothioate ($PhSO_2SPh$) were also determined by comparison of their mass spectra with those on the available NIST database.

Synthesis of Diphenyl Sulfoxide (Ph_2SO) by Friedel–Crafts Reactions

Method (1). To an approximately 2:1 (molar ratio) liquid mixture of PhH (2.00 g, 25.6 mmol) and $SOCl_2$ (1.45 g, 12.2 mmol), which had been maintained at about 70°C using a hot-water bath, granular $AlCl_3$ (1.63 g, 12.2 mmol) was added in aliquots (piecewise) as follows (experiment performed in a fumehood): First, one piece of $AlCl_3$ was added to the PhH–$SOCl_2$ mixture, and gas (HCl) bubbles started to form immediately. The piece of $AlCl_3$ was crushed using a stirring rod. When most of the piece of $AlCl_3$ had dissolved and bubbling occurred very slowly, another piece of $AlCl_3$ was added. Each piece of $AlCl_3$ was crushed before the next piece was added. All the $AlCl_3$ granules were eventually added at 70°C into the PhH–$SOCl_2$ mixture piece by piece. In the beginning of the reaction, the solution was light green. It turned dark green as the reaction went to completion, which was indicated by ceasing of bubbling after all the $AlCl_3$ had been added. Then water (40 mL) was poured into the reaction mixture, and the green color disappeared. This was followed by addition of diethyl ether (20 mL). All the contents were transferred into a separatory 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. The diethyl ether was evaporated. A white crystalline product Ph_2SO (2.10 g, 10.4 mmol) was received in an isolated yield of 85%. The product was characterized by GC-MS, showing that it only contained a sole compound Ph_2SO with a purity of 99.9%.[14]

The reactions were also performed at room and ice-water temperatures (about 25°C and 0°C, respectively) by mixing the starting materials $PhH{:}SOCl_2{:}AlCl_3 = 2{:}1{:}1$ (molar ratio) in the same manner. GC-MS showed that the product (after aqueous work-up) from each experiment contained Ph_2SO (Yield: about 75%), the major component, and Ph_2S (yield: 3–5%], $PhSO_2SPh$ (yield: about 5%), and (Ph_2SO_2) (trace amount), the minor components.

Method (2). Synthesis of Ph_2SO was also performed under modified conditions as follows: With constant stirring, $SOCl_2$ (1.75 g, 14.7 mmol) was added in aliquots (dropwise) to an approximately 2:1 (molar ratio) mixture of PhH (2.41g, 30.9 mmol) and $AlCl_3$ (1.96 g, 14.7 mmol) at about 25°C. The reaction took place quickly, as indicated by bubbling as above. After all the $SOCl_2$ was added, the reaction went to completion, which was indicated by cessation of bubbling. Then aqueous workup was performed as above. Eventually, a white crystalline product Ph_2SO (2.30 g, 11.4 mmol) was received in an isolated yield of 78%. GC-MS showed that the product contained essentially a sole compound Ph_2SO with the purity of 99%.[14]

For a reaction performed at 0°C in the same manner, GC-MS showed that the product contained Ph_2SO (yield: 72%) as the major component and Ph_2S (yield: 6%), $PhSO_2SPh$ (yield: about 5%), and Ph_2SO_2 (trace amount) as the minor components.

Attempted Synthesis of Diphenyl Sulfide (Ph_2S) by $AlCl_3$-Facilitated Reaction of PhH and $SOCl_2$

PhH (2.36 g, 30.2 mmol) was poured all at once into a 1:1 (molar ratio) mixture of $SOCl_2$ (1.71 g, 14.4 mmol) and $AlCl_3$ (1.92 g, 14.4 mmol), which had been maintained at about 0°C using an ice-water bath. The contents were stirred at 0°C. The reaction took place quickly, indicated by bubbling as above. After the reaction went to completion, which was indicated by cessation of bubbling, an aqueous workup was performed as above. The ether solvent was allowed to evaporate completely. A very slightly yellow liquid (1.76 g) was received. The product was determined by GC-MS to contain Ph_2S (yield: 37%) and Ph_2SO (yield: 27%).[15] In addition, a small amount of $PhSO_2SPh$ (yield: about 5%) and a trace amount of $PhSO_2Ph$ were identified by GC-MS.

For a reaction performed at 25°C in the same manner, GC-MS showed that the product contained Ph_2SO (yield: 52%) as the major component and Ph_2S (yield: 22%), $PhSO_2SPh$ (yield: about 5%), and $PhSO_2Ph$ (trace amount) as the minor components.

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14. Purity of the Ph_2SO product was determined by comparison of the Ph_2SO peak area to the tiny impurity (Ph_2S) peak area. No other impurities were found in GC-MS.
15. The molar ratio of Ph_2S:Ph_2SO in the isolated product (1.76 g) was determined to be 1.4:1 by comparison of the related GC peak areas. Ph_2S (37%) and Ph_2SO (27%), the percent yields based on the quantity of $SOCl_2$, were determined according to the total quantity of the isolated product (1.76 g) and the Ph_2S:Ph_2SO molar ratio (1.4:1) in the product. By comparison of the $PhSO_2SPh$ GC peak area with that for Ph_2SO, the yield of $PhSO_2SPh$ in this and all the other samples containing it was estimated to be about 5%.