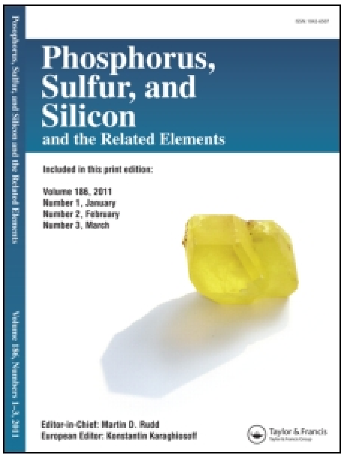

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Triethylhydrogenammonium chloride-XAlCl$_3$ Ionic Liquids (ILs) were used as a catalyst for the clean synthesis of dichlorophenylphosphine sulfide. Two synthesis routes were investigated; one of them was a reaction of sulfur and Dichlorophenylphosphine (DCPP), and another was a one-pot reaction of benzene, phosphorus, chloride, and sulfur. Effects of the ILs composition and reaction time and the quantity of the ILs on the reactions were studied. A simple product isolation procedure was achieved. The ILs showed reusable and low-consumption characters in the reaction of sulfur and DCPP. Thus the triethylhydrogenammonium chloride-XAlCl$_3$ ILs gave this reaction a green character.

Keywords Clean synthesis; Dichlorophenylphosphine sulfide; ionic liquids; Lewis acid

INTRODUCTION

Dichlorophenylphosphine Sulfide (DCPPS) is an important industrial material that is widely used in the manufacture of flameretardants, insecticides, and plasticizers. There are many literatures discovering various ways for its preparation. Among these methods, there are two that are commonly discussed. One is that the reaction mixture of benzene and phosphorus trichloride (PCl$_3$) catalyzed by aluminium chloride (AlCl$_3$) at the first step was then sulfurized without isolation of the catalyst.[1] In this method, the catalyst consumption is large and nonreusable, and the DCPPS has to be isolated by hydrolysis, which will contaminate the environment. The other commonly used method to prepare DCPPS is to react phosphorus thiochloride and benzene catalyzed

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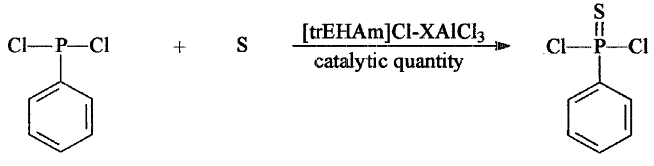
by a Lewis acid.[2–6] With this method, there still are some problems of large catalyst consumption and difficulty in isolation, and in some cases, high temperature and pressure was involved.[2,3] Therefore, there is a strong incentive to find a convenient and clean synthesis to prepare DCPPS.

Recently, Ionic Liquids (ILs) are receiving an upsurge of interest as green solvents or catalysts, and they are widely studied as replacements for conventional media in chemical proceses. There are literatures discovering that the aluminum halide-alkylammonium halide ILs can replace the Lewis-acid catalyzed reactions, such as a Friedel-Crafts reaction, and show green characters; they are free of volatile organic compounds; they can be readily recycled; they have profound effects on the activity and selectivity in reactions, and, in most of the cases, they facilitate product isolation.[7,8] In previous reports, we found [BuPy]Cl-$AlCl_3$ (BuPy = N-butylpyridinium cation),[9] [trEHA]Cl-$XAlCl_3$ (trEHAm = triethylhydrogenammonium cation),[10] and Et_4NBr-$XAlCl_3$ (Et_4NBr = tetraethylammonium bromide)[11] ILs (where X is the mole ratio of $AlCl_3$ in the IL) could catalyze the Friedel-Crafts reaction of PCl_3 and benzene and render this reaction cleaner characters. We are wondering if ILs could replace the Lewis acid in the preparation of DCPPS and render the reaction a clean synthesis and convenient isolation procedure.

In this article; we use the readily prepared ILs [trEHAm]Cl-$XAlCl_3$ to catalyze the reaction of sulfur and dichlorophenylphosphine via an one-pot reaction to prepare DCPPS (see Scheme 1). Effects of the quantity of ILs used, the composition of the ILs (different X values), and reaction time were investigated. ILs were recycled, and their reusability was also investigated.



SCHEME 1

EXPERIMENTAL

Materials

Triethylhydrogenammonium chloride ([trEHAm]Cl), phosphorus trichloride, aluminum chloride, sulfur, and petroleum ether (60–90°C) were all from VAS Chemical Reagent Corporation Ltd. in Beijing.

Dichlorophenylphosphine was prepared according to our previous described procedures.[11] To ensure reaction conditions were free of water, the preparation of ILs and sulfurization were carried out in a nitrogen atmosphere.

Preparation of [trEHAm]Cl-2AlCl$_3$ ILs

In a round-bottomed flask equipped with a magnetic stirrer and a gas inlet valve, 26.67 g (0.2 mol) anhydrous AlCl$_3$ was slowly added to 13.8 g (0.1 mol) triethylhydrogenammonium chloride. The mixture was stirred for 3 h to ensure a complete reaction. Other compositions of [trEHAm]Cl-XAlCl$_3$ ($X = 1$, 1.5, 2.3) were prepared according to the previously discussed procedure, with appropriate amounts of AlCl$_3$ and triethylhydrogenammonium chloride.

Preparation of DCPPS from PCl$_3$, Benzene, and Sulfur

Benzene 65 g (0.833 mol) was added dropwise to a refluxing mixture of PCl$_3$ 343.7 g (2.5 mol) and [trEHAm]Cl-2AlCl$_3$ 30.8 g (0.076 mol) for 1 h and then was refluxed at 78–80°C for 4 h. The mixture was then cooled to r.t.; the stirrer was stopped, and then the solution was settled for 30 min; a biphasic system was obtained (in the case of ^{31}P, it was necessary to measure NMR, and the clear upper portion of the solution was withdrawn to another measuring flask). The solution was then stirred and heated to distill the excess PCl$_3$ at 40°C and reduce pressure. Then the residue was cooled to 30°C, and 28.4 g sulfur powder (0.887 mol) was added partially to keep the reaction at about 80°C. After the addition of the sulfur, the mixture was reacted for 1.5 h at 80°C. Then the reaction mixture was cooled, and petroleum ether was added to the solution and stirred for 30 min in order to extract the DCPPS. After the stirrer was stopped, phase separation was observed. The upper layer was the petroleum ether phase, and the lower layer was the IL phase. The DCPPS was partially dissolved in the petroleum ether. The petroleum-ether layer was separated and collected. The operation was repeated thrice, and the collected petroleum ether was combined. Then the ILS in the lower layer were separated and saved for another reaction. The rough DCPPS-petroleum ether solution was then washed with cold water to remove the unreacted Dichlorophenylphosphine (DCPP) and was dried with anhydrous CaCl$_2$. The petroleum ether in the organic layer was then recovered by distillation at atmospheric pressure at first and then at reduced pressure. The DCPPS yield 68% based on benzene was distilled in reduced pressure with b.p. temperature 105°C at 267 Pa and 150°C at 1333 Pa, respectively (literature 150°C/3.47 kPa.[12]

95–110°C/0.27–0.40 kPa,[1,2] 87–88°C/0.40 kPa.[17] 76–77°C/0.08 kPa[14]). Density at 25°C (d_{25}) was 1.390 (g/cm3) (literature,[13] $d_{20} = 1.4042$). Reflection index (n_D^{20}) was 1.6178–1.6182 (literature,[13] $n_D^{20} = 1.6250$). Elemental analysis: experimental value of elemental content, %: Cl, 33.94; S, 15.01; C, 34.31; H, 2.55. Calculated value: Cl, 33.64; S, 15.16; C, 34.12; H, 2.37. Figure 1 shows the flowing chart and material conservation of the previously discussed procedure.

Preparation of DCPPS from DCPP and Sulfur

In a round-bottomed four-necked flask equipped with a stirrer, a thermometer, and a gas inlet valve, the designed amount of DCPP was added to a weighed quantity of [trEHAm]Cl-XAlCl$_3$. The mixture was heated to 30°C, and an equal mole of sulfur based on the DCPP was added. The reaction was exothermic, and sulfur was added partially to keep the reaction temperature between 30–40°C. After addition of sulfur, the reaction was kept for the scheduled time. Then the reaction mixture was cooled, petroleum ether was added to extract the DCPPS thrice, and the petroleum ether layers were combined. The rough DCPPS-petroleum ether solution was then washed with cold water to remove the unreacted DCPP and was dried with anhydrous $CaCl_2$. The low-boiling liquid in the upper layer was removed by distillation at atmospheric pressure; DCPPS was received using the method previously discussed. The yield was calculated based on DCPP.

The IL recovered in the lower layer was separated and saved for another reaction. Before use, the IL was kept at 60°C at reduced pressure for about 1 h to remove the dissolved petroleum ether.

RESULTS AND DISCUSSION

^{31}P NMR Analysis

The ^{31}P NMR analysis was carried out for the solution sampled in the preparation of DCPPS from PCl_3, benzene, and sulfur. Chemical shifts are referenced to 85% H_3PO_4, with positive values downfield. The original ^{31}P NMR signal of the PCl_3 was detected at $\delta + 221.2$ ppm (literature 221 ppm). A signal that belonged to DCPP at δ 162.4 ppm (literature[15] 161.2 ppm) was also detected from this solution. In our previous work,[11] we have shown that the complex (DCPP $\cdot$ AlCl$_3$) was not dissolved in either PCl_3 or petroleum ether. It agrees with the ^{31}P NMR analysis results obtained in this work. The complex (DCPP $\cdot$ AlCl$_3$) formed during the reaction in the IL phase was dissociated by an$[AlCl_4]^-$ anion. This helped the DCPP to be dissolved into the PCl_3 Phase. A sample

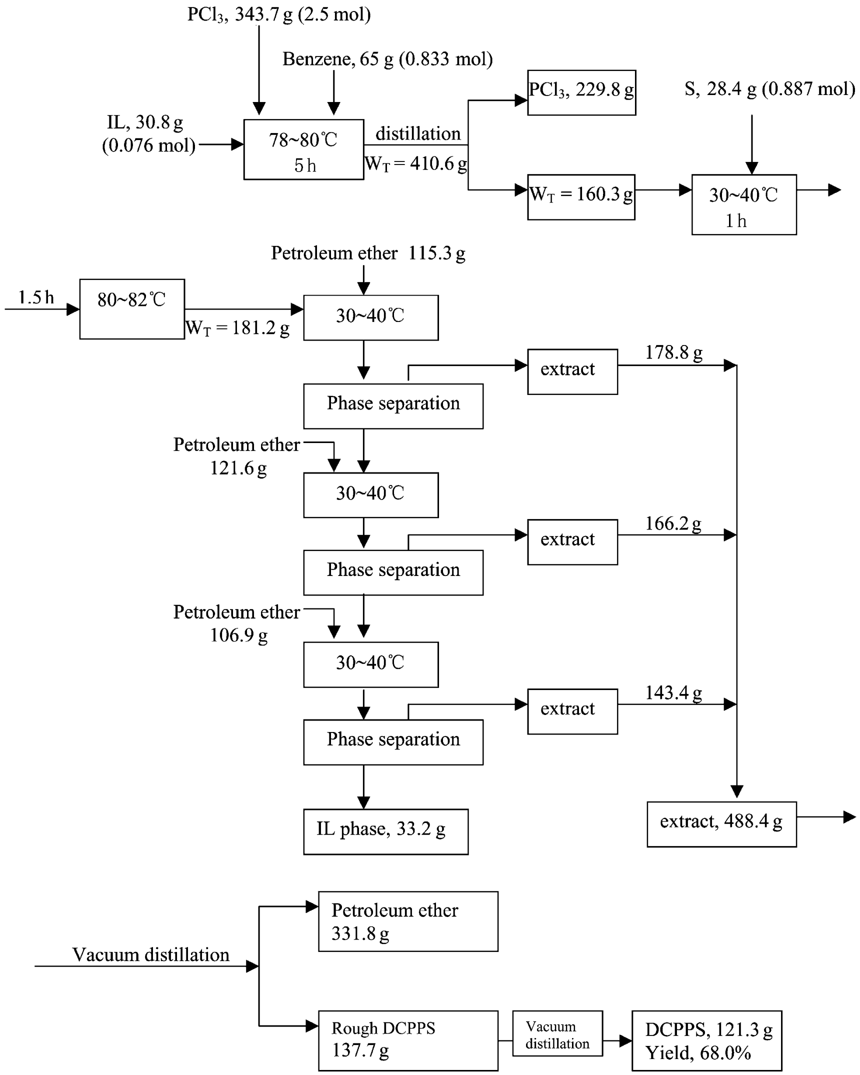
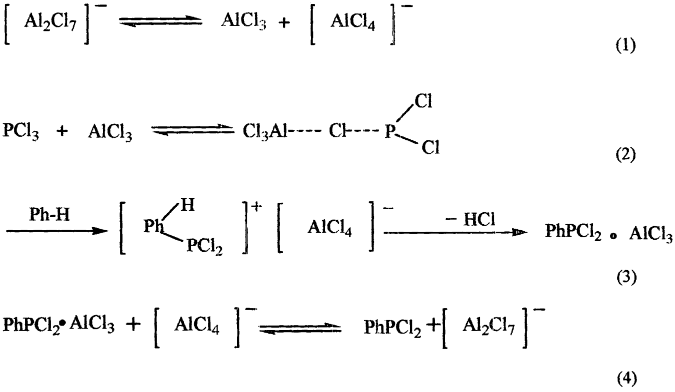


FIGURE 1 Flowing chart of DCPPS synthesis from phosphorus trichloride, benzene, and sulfur catalyzed with triethylhydrogenammonium chloride-$2AlCl_3$ IL with PCl_3:benzene:sulfur:IL = 33:11:11:1 (molar ratio).

from a solution prepared from 1 mol PCl_3 and 0.33 mol $AlCl_3$ was also determined by the ^{31}P NMR; three signals were observed. The strong signal at $\delta + 221.2$ ppm assigned to PCl_3 was obvious, while the two weak signals $\delta + 106.0$ and $\delta + 37.8$ were assigned to the interaction of PCl_3 with $AlCl_3$; one belonged to $Cl_3P—AlCl_3$, and another belonged to

Cl_2P—Cl—$AlCl_3$. These NMR assignments corresponding to two forms of a $PCl_3/AlCl_3$ interaction were not reported in the literature. Therefore, one of the mechanisms can be assumed that the $AlCl_3$-PCl_3 interaction formed an ionic complex (Cl_2P^+ $AlCl_4^-$), and that the cation was the species attacting the aromatics. The mechanisms of the Friedel–crafts reaction of the phosphylation of benzene catalyzed by the [trEHAm]Cl-$2AlCl_3$ IL can assumed as in Scheme 2.



SCHEME 2

Catalytic Activity

This study showed that the reaction of sulfur and DCPP would not take place without a catalyst. While the reactions using the [trEHAm]Cl-$2AlCl_3$ ILs as a catalyst proceeded smoothly. In the one-pot reaction using PCl_3, benzene, and sulfur as raw materials, we found that the acidic ILs catalyzed the reaction with yields of about 60%~78%, while the basic and neutral ILs showed nearly no catalytic activity. It was found that a small amount of ILs catalyzed the reaction with fair yields. For example, with PCl_3:benzene:sulfur:ILs = 3:1:1:0.08, a yield of 62.1% DCPPS was received. A yield of 78.8% was obtained in the case of a 10:10:1 mole ratio of DCPP:sulfur:ILs, and a yield of 70.0% was obtained in the case of a 30:30:1 mole ratio of DCPP:sulfur:ILs. Another interesting result is that the use of large mole ratios of ILs decreased the yields. The ILs layers were weighed after each reaction and distillation. The weight of the residue of the IL's layer was increased as compared with the weight of the catalyst, and the amount of increase showed a direct ratio to the amount of ILs used in the reactions. We believe that the product was dissolved in the ILs, since the ILs were miscible with DCPPS. Benzene

TABLE I Catalytic Activity of [trEHAm]Cl-XAlCl$_3$ ILs[a]

X	DCPP:S:ILs/mole ratio	Yield (%)
1	10:10:1	8.6
1.5	3:3:1	10.6
1.5	5:5:1	24.1
1.5	10:10:1	63.8
1.5	15:15:1	69.4
1.5	30:30:1	66.1
2	3:3:1	23.7
2	5:5:1	37.6
2	10:10:1	78.8
2	15:15:1	70.2
2	30:30:1	70.0
2.3	3:3:1	32.6
2.3	5:5:1	41.2
2.3	10:10:1	84.3
2.3	15:15:1	76.9
2.3	30:30:1	74.5

[a] Reactions were completed at 40°C for 5 min.

and PCl$_3$ were partially miscible, and petroleum ether was immiscible with ILs.[16]

Reaction cases using various amounts of ILs with different ILs compositions (a different X value in [trEHAm]Cl-XAlCl$_3$ ILs) were carried out to investigate the catalytic activity of [trEHAm]Cl-XAlCl$_3$ ILs in the reaction of DCPP and sulfur, and the results are summarized in Table I.

The acidic ($X > 1$) [trEHAm]Cl-XAlCl$_3$ ILs showed fair catalytic activity in the reaction; the catalytic activity increased as their acidity increased. Those basic ($X = 0.67$) and neutral ($X = 1$) [trEHAm]Cl-XAlCl$_3$ ILs, however, showed nearly no catalytic activity.

Product Isolation

In all cases, DCPPS was extracted directly from the reaction mixture. This isolation method is different from those in the literature. In the preparation methods using AlCl$_3$ as a catalyst and PCl$_3$ and benzene as starting materials, the DCPPS was not isolated directly, and the reaction mixtures had to be hydrolyzed in ice water. Thus the isolation procedures in our experiments provide a more convenient and more environmental way to get the product. It is apparent that the DCPPS was not in the complex form with AlCl$_3$ because the Lewis bacity of DCPPS was lower than DCPP.

TABLE II Effects of Reaction Time and Temperature[a]

Temperature (°C)	Reaction time (min)	Yield (%)
30–40	10	79.3
30–40	15	77.5
30–40	30	79.6
50–60	10	78.1
50–60	15	80.2
50–60	30	78.3
70–80	10	78.5
70–80	15	79.2
70–80	30	80.4

[a] DCPP:S:ILs($X = 2$) = 10:10:1.

Effects of Reaction Time and Temperature

The effects of reaction time and temperature on the reaction of DCPP and sulfur were investigated, and the results were summarized in Table II.

From Table II it is shown that the reaction was completed at a low temperature and in short time. This is different from that described in the literature. In the literature methods, reactions were carried out at about 80°C in about 3 h. The reaction in our experiments took place at about 30–40°C and were be completed within 10 min after an addition of sulfur. A lower reaction temperature and shorter reaction time in this reaction showed good catalysis activity of the ILs.

TABLE III Reusable Characters of [trEHAm]Cl-2AlCl$_3$ ILs

DCPP:S:ILs (mole ratio)	Runs[a]	Yield (%)
10:10:1	1	78.8
	2	77.7
	3	78.4
	4	76.6
	5	77.8
	6	73.6
15:15:1	1	70.3
	2	71.2
	3	71.4
	4	69.6
	5	67.4
	6	70.2

[a] Reactions were carried out at 30–40°C for 5 min.

Reusable Character of ILs

The isolated ILs were used directly in the followed runs to investigate their reusable characters, and the results are summarized in Table III. From Table III it can be seen that the ILs still showed good catalytic activity, as they were used another 5 times, which means the ILs can be recycled. Thus a yield of 78.8% was obtained in the first run (with DCPP:S:ILs equal to 10:10:1) and a yield of 76.7% was obtained at the sixth reaction when the ILs were reused. In the preparation of DCPPS directly from PCl_3, benzene, and sulfur, similar results were obtained. While in preparation of DCPP from benzene and PCl_3 with the catalysis of same ILs, after the catalyst was recycled three times, no activity was observed.

CONCLUSIONS

[trEHAm]Cl-XAlCl$_3$ ILs were used as a catalyst for the clean synthesis DCPPS from the reaction of sulfur and DCPP and from the one-pot reaction of benzene, phosphorus trichloride, and sulfur. A simple product isolation procedure was achieved. The experimental phenomenon indicated that the DCPPS did not form a complex in the [trEHAm]Cl-XAlCl$_3$ ILs but only simply dissolved in it. The effects of the IL's composition and reaction time and the quantity of the ILs on the reactions were studied. The ILs showed reusable, low consumption, and high activity characters in the reaction of sulfur and DCPP. Thus [trEHAm]Cl-XAlCl$_3$ ILs gave this reaction a green character. Compared with literature methods for the preparation of DCPPS, the reaction using [trEHAm]Cl-XAlCl$_3$ ILs as a catalyst exhibited a simple product isolation procedure, a short reaction time, and less and reusable catalyst consumption, which contribute to a clean synthesis of DCPPS.

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