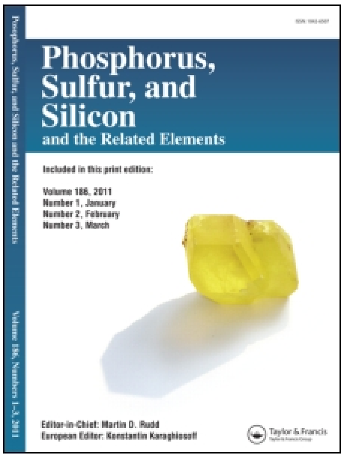

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Synthesis of Dichlorophenylphosphine via a Friedel-Crafts Reaction in $[Et_4N]Br\text{-}XAlCl_3$ Ionic Liquids

Yu-Yong Wu[a]; Li-Sheng Wang[a]; Zhong-Wei Wang[a]
[a] School of Chemical and Environment Engineering, Beijing Institute of Technology, Beijing, People's Republic of China

To cite this Article Wu, Yu-Yong , Wang, Li-Sheng and Wang, Zhong-Wei(2005) 'Synthesis of Dichlorophenylphosphine via a Friedel-Crafts Reaction in $[Et_4N]Br\text{-}XAlCl_3$ Ionic Liquids', Phosphorus, Sulfur, and Silicon and the Related Elements, 180: 12, 2667 — 2677

To link to this Article: DOI: 10.1080/104265090930407

URL: http://dx.doi.org/10.1080/104265090930407

Phosphorus, Sulfur, and Silicon, 180:2667–2677, 2005
Copyright © Taylor & Francis Inc.
ISSN: 1042-6507 print / 1563-5325 online
DOI: 10.1080/104265090930407

Synthesis of Dichlorophenylphosphine via a Friedel-Crafts Reaction in $[Et_4N]Br$-$XAlCl_3$ Ionic Liquids

Yu-Yong Wu
Li-Sheng Wang
Zhong-Wei Wang
School of Chemical and Environment Engineering,
Beijing Institute of Technology, Beijing, People's Republic of China

The Friedel-Crafts reaction of phosphorus trichloride and benzene in $[Et_4N]Br$-$XAlCl_3$ *(*$[Et_4N]Br$ *= tetraethylammonium bromide) ionic liquids (ILs) was investigated for the clean synthesis of dichlorophenylphosphine (DCPP). A simple product isolation procedure was achieved, and the effects of IL's composition, reaction time, and quantity on this reaction were studied. The* $[Et_4N]Br$-$XAlCl_3$ *ILs gave this reaction a green character. From the isolation experiments, it was found that (a) because of the formation of the complex of DCPP and* $AlCl_3$*, the catalytic activity of the* $[Et_3NH]Cl$-$XAlCl_3$ *(*$[Et_3NH]Cl$ *= triethylhydrogenamonium chloride) was reduced; (b) with the addition of quaternary ammonium to the IL's residue, additional DCPP could be recovered.*

Keywords Dichlorophenylphosphine; Friedel-Crafts reaction; ionic liquids; clean synthesis

INTRODUCTION

Dichlorophenylphosphine (DCPP) is a commercially important compound in organic synthesis and it is widely used in the preparation of flame-retardants, insecticides, stabilizers, plasticizers, and antioxidants. It can be prepared by an aluminum trichloride ($AlCl_3$)-catalyzed Friedel-Crafts reaction of benzene with PCl_3.[1] However, there exist problems in the preparation procedure. Because of the formation of complex of $AlCl_3$ and DCPP in the reaction, a stoichiometric or excess amount of $AlCl_3$ is needed and it makes the DCPP difficult to be isolated. In those modified methods,[2–5] $POCl_3$, pyridine, or water were

Received September 14, 2004; accepted December 18, 2004.

Address correspondence to Li-Sheng Wang, Beijing Institute of Technology, School of Chemical and Environment Engineering, Beijing 100081, People's Republic of China. E-mail: lishengwang@btamail.net.cn

added to breakdown the complex, and then the DCPP was extracted using organic solvents for the isolation of the product. This procedure adds the to cost and need for more industrial procedures. The non-reusable and large quantity of a catalyst would form a great amount of solid waste, which is difficult to handle and can greatly contaminate the environment. Moreover, in the extraction procedure, a large quantity of organic solvents is needed, which is another source that contaminates the environment. Therefore, there is a strong incentive to find clean synthesis and simple product isolation procedures in the preparation of DCPP.

Ionic liquids (ILs) exhibit various advantages in organic reactions.[6–9] The designable ILs possesses green characters: They are free of volatile organic compounds (VOCs); they are readily recycled; and they have profound effects on the activity and selectivity in reactions. In most cases of the Friedel-Crafts reactions, the using of aluminate ionic liquids facilitates the isolation of products.

In a previous report,[10] we found [BuPy]Cl-X$AlCl_3$ ([BuPy]Cl = N-butylpyridinium chloride; X is the mole ratio of $AlCl_3$ in the [BuPy]Cl and $AlCl_3$ system) ionic liquid could catalyze the Friedel-Crafts reaction of PCl_3 and benzene, and render this reaction some cleaner characters, such as less catalyst consumption, convenient catalyst recovery, and product isolation. After the reaction, the mixture was homogeneous at room temperature; the DCPP was extracted using petroleum ether that was immiscible with the ILs. In an alternative report,[11] we used $[Et_3NH]Cl$-X$AlCl_3$ ($[Et_3NH]Cl$ = triethylhydrogenammonium chloride; X is the mole ratio of $AlCl_3$ in the $[Et_3NH]Cl$ and $AlCl_3$ system) ionic liquid to catalyze the same reaction, and, in this case, we found that at a high temperature, the reaction mixture was almost homogeneous; after the reaction, the mixture was cooled to room temperature. It separated into a diphase system. Part of the DCPP could be separated from the PCl_3 layer directly by distillation, and another part was extracted from the ILs layer using petroleum ether as solvent. These experiments demonstrate that the solvent properties had been changed with the changing of the molecular structure of the cation. Moreover, we found that for the IL's phase in the both cases, after the recovery of petroleum ether by vacuum distillation, the weight of the IL's residue was obviously increased because of the formation of the complex of DCPP and $AlCl_3$. From a point of view of the product isolation and the catalyst or raw materials recycling, this reaction needs to be improved.

This article is our continuous study of ILs catalyzed reaction of PCl_3 and benzene. The reaction characters of PCl_3 and benzene using another ILs $[Et_4N]Br$-X$AlCl_3$ ($[Et_4N]Br$ = tetraethylammonium bromide; X is the mole ratio of $AlCl_3$ in the $[Et_4N]Br$ and $AlCl_3$ system), as catalyst was investigated.

$$PCl_3 + Ph\text{-}H \xrightarrow{[Et_4N]Br\text{-}XAlCl_3} PhPCl_2 \qquad (1)$$

The effects of changing the anion on the catalyst recycling and product isolation will be investigated in this article. The effects of acidity (different X values), the amount of the $[Et_4N]Br\text{-}XAlCl_3$ ILs, and the effects of reaction time and reactant composition on this reaction will be studied as well. A more convenient isolation procedure from the reaction mixture successfully is achieved and the separation of the DCPP from the ILs was compared with the separation from complex $AlCl_3\cdot$ DCPP.

EXPERIMENTAL

Aluminum chloride, phosphorus chloride, triethylhydrogenammonium chloride ($[Et_3NH]Cl$), tetraethylammonium bromide ($[Et_4N]Br$), petroleum ether (60–90°C), and benzene were analytical reagents from VAS Chemical Reagent Corporation Ltd. in Beijing, China. $[Et_3NH]Cl\text{-}AlCl_3$ ionic liquids were prepared according to the previous procedure we described.

To ensure reaction conditions were free of water, the preparation of ILs and the Friedel-Crafts reaction were carried out in a nitrogen atmosphere.

Preparation of $[Et_4N]Br\text{-}XAlCl_3$ and $[Et_3NH]Cl\text{-}XAlCl_3$ ($X = 2$) ILs

In a round-bottomed flask equipped with a magnetic stirrer and a gas inlet valve, 26.7 g (0.2 mol) of anhydrous $AlCl_3$ was slowly added to 21.0 g (0.1 mol) of tetraethylammonium bromide. The mixture was stirred for 3 h to ensure a complete reaction, and reduced pressure (13.3 kPa) was used to remove the possible evaporate impurities.

Similarly, to prepare a $[Et_3NH]Cl\text{-}2AlCl_3$ ionic liquid, 0.2 mol anhydrous $AlCl_3$ was slowly added to 0.1 mol triethylammonium hydrogen chloride, and the mixture was stirred for 3 h to ensure a complete reaction.

Other compositions of $[Et_4N]Br\text{-}XAlCl_3$ and $[Et_3NH]Cl\text{-}XAlCl_3$ ($X = 1, 1.5, 2.5$ mole ratio of $AlCl_3$) were prepared according to this procedure, with appropriate amounts of $AlCl_3$, tetraethylammonium bromide, and triethylammonium hydrogen chloride (for example, 0.1 mol $AlCl_3$ and 0.1 mol $[Et_4N]Br$ for $X = 1$; 0.15 mol $AlCl_3$ and 0.1 mol $[Et_4N]Br$ for $X = 1.5$; 0.25 mol $AlCl_3$ and 0.1 mol $[Et_4N]Br$ for $X = 2.5$).

General Friedel-Crafts Reaction Procedure

In a round-bottomed four-necked flask equipped with a stirrer, a condenser, and a gas inlet valve, the designed amount of PCl_3 and benzene were added to a weighed quantity of $[Et_4N]Br\text{-}XAlCl_3$. The mixture was heated and refluxed for the scheduled number of hours. Then the mixture was cooled to about 20°C and phase separation could be observed. The lower layer was viscous IL and the upper layer was a mixture of PCl_3, benzene, and DCPP. The product DCPP in the lower layer was recovered in a similar way as described in our previous article.[11] Extract the DCPP in the ILs with petroleum and then get the product at reduced pressure. The PCl_3 and benzene in the upper layer was removed by distillation at atmospheric pressure, followed by distillation at a slightly reduced pressure (6.67 kPa) below 90°C. The DCPP was distilled in vacuum with a boiling point of 92–94°C/1.56 kPa (literature 90–92°C/1.33 kPa,[14] 68–70°C/0.133 kPa,[14] 94°C/1.60 kPa)[12] density d_{30} 1.3576–1.3682 (literature, d_{25} 1.327 g/mL,[14] $d_{30.9}$ 1.3567 g/mL),[13] viscosity η_{30} 3.01 mPa·s (literature $\eta_{29.45}$ 2.99 mPa·s),[13] refraction index n_D^{25} 1.5910–1.5914 (literature n_D^{25} 1.5912).[14] Gas chromatographic analysis (GC-14C gas chromatograph) showed that the purity of DCPP was above 96.0%.

Preparation of Complex $AlCl^3$·DCPP and the Isolation of DCPP From the Complex of DCPP and $AlCl_3$

The complex used for the DCPP isolation experiments was prepared by mixing DCPP with an equal molar of $AlCl_3$. The mixture was kept at 70°C for 2 h. To 62.4 g (0.2 mole) of the complex prepared above was added to 27.5 g (0.2 mole) and $[Et_3NH]Cl$ (the reaction is exothermic and the $[Et_3NH]Cl$ should be added in portions), and the mixture was kept at about 70°C for 2 h. DCPP was extracted with petroleum ether or PCl_3 and isolated in a similar way as in the above general procedure to prepare DCPP. In other cases, the above procedure was repeated, except for replacing the $[Et_3NH]Cl$ with an equimolar of $[Et_4N]Br$.

RESULTS AND DISCUSSIONS

Isolation of DCPP From the $[Et_4N]Br\text{-}XAlCl_3$ Catalyzed Reaction Mixture

A more convenient product isolation procedure was achieved and the amount of the complex of DCPP and $AlCl_3$ in the ionic liquid residue was reduced. Because there exists an excess amount of PCl_3, the reaction mixture was separated into a diphase system. Although PCl_3 is extremely soluble in the ionic liquid, the reverse is not the case, with no appreciable IL solubilization in the PCl_3 phase. Therefore, the leaching of a catalyst into the PCl_3 phase can be minimized. The product DCPP could be isolated without using any other organic solvent, which is more convenient in industrial processes, compared with classical methods, and makes the PCl_3 and benzene readily to be recycled. In all cases, the yields of DCPP isolated from the reaction mixture ranged from 46–60% (based on benzene).

Catalytic Activity of $[Et_4N]Br\text{-}XAlCl_3$ Ionic Liquids

Reaction cases using various amounts of IL's with different IL's compositions (a different X value in $[Et_4N]Br\text{-}XAlCl_3$ ionic liquids) were carried out to investigate the catalytic activity of $[Et_4N]Br\text{-}XAlCl_3$ ILs in the reaction of PCl_3 and benzene. The results are summarized in Table I. From Table I we can find that $[AlCl_3Br]^-$ does not catalyze the reaction (when X = 1) and excess $AlCl_3$ is needed to catalyze the reaction. Thus, the acidic ($X > 1$) $[Et_4N]Br\text{-}XAlCl_3$ ILs showed fair catalytic activity in the reaction, and the catalytic activity increased as their acidity increased. Those basic ($X = 0.67$) and neutral ($X = 1$) $[Et_4N]Br\text{-}XAlCl_3$ ILs, however, showed nearly no catalytic activity. These results agree with those discovered Friedel-Crafts reactions catalyzed by other ILs.[11] The most interesting result in these cases is that the ILs could be used

TABLE I Catalytic Activity of $[Et_4N]Br\text{-}XAlCl_3$ ILs. Reactions were Carried out with Refluxing for 6 h

X	PCl_3:benzene:ILs/mole ratio	Yield/%
0.67	4:2:1	3.2
1	4:2:1	5.4
2	4:2:1	23.6
2	8:4:1	44.0
2	16:8:1	50.4
1.5	30:10:1	49.6
1.5	30:15:1	46.9
2	30:15:1	51.2
2.2	30:15:1	55.4
2	30:10:1	55.1
2.2	30:10:1	59.9
1.5	60:30:1	24.8
2	60:30:1	27.2
2.2	60:30:1	19.5

in catalytic quantity. Thus, a yield of 51.2% was obtained in the case with the 30:15:1 mole ratio of PCl_3:benzene:ILs (X = 2). We were interested to find that when the ionic liquids used in a catalytic amount (a mole ratio of benzene:ILs exceed 10:1), the amount of product isolated showed a direct ratio to the amount of the ILs. When a large amount of ionic liquids were used, the yields decreased.

Compared with the normal method to prepare DCPP using $AlCl_3$ as a catalyst, which was near 80%, the yield using ionic liquids is fairly lower. However, in the normal system, the catalyst consummation is much more, compared with the IL's catalyzed reaction. From a point of view of reactant recycling, the unreacted benzene and PCl_3 are easily recovered by simple evaporation after the reaction and the phase separation, while the $AlCl_3$ is wasted after the reaction, and the $AlCl_3$ takes the most expense in the production of DCPP. If we define a quantity (C) to represent how much moles of DCPP are produced with one mole of $AlCl_3$, we can find that, in the normal process using $AlCl_3$ as catalyst, this quantity is always less then its unity. However, when using ILs as a catalyst, this quantity is larger than its unity. From Table II, it is clear that the cost of using a normal $AlCl_3$ as a catalyst can be five times as high than using ILs as catalyst; and the contamination must also be five times reduced by using ILs. Thus, use of ILs as a catalyst has the advantage of less catalyst consumption, and, therefore, brings out less waste, which makes it interesting.

Effects of Reactant Composition and Reaction Time

The effects of reactant composition and reaction time on the reaction of PCl_3 and benzene using a catalytic quantity of $[Et_4N]Br\text{-}XAlCl_3$ were

TABLE II Effects of Reactant Composition and Reaction Time

PCl_3:benzene: [a]ILs/mole ratio	Reaction time/h	Yield/%	C.
30:10:1	4	48.8	2.44
30:10:1	6	55.1	2.76
30:10:1	8	56.6	2.83
30:15:1	4	44.5	3.34
30:15:1	6	51.2	3.84
30:15:1	10	53.1	3.98
60:30:1	6	27.2	4.08
60:30:1	10	29.3	4.40
60:30:1	16	28.1	4.22

[a] ILs: $[Et_4N]Br\text{-}2AlCl_3$.

investigated, and the results were summarized in Table II. From Table II, we found that the yields showed a slightly increased trend when the mole ratio of PCl_3:benzene increased. Six hours would be enough for the reaction to be complete, and a longer time than that did not show as apparent increase of the yields. Thus, with a catalytic quantity of ILs, the mole ratio of PCl_3:benzene:ILs (X = 2) is 30:15:1; when the reaction time is 4 h, a yield of 44.5% is obtained, while when the reaction time is 6 h, the yield is 51.2%, and when the reaction time is 10 h, the yield is 53.1%.

Reusable Character of the $[Et_4N]Br\text{-}XAlCl_3$ ILs

The catalytic amount of ILs was isolated and used directly in the followed runs to investigate their reusable characters. From Table III, we found that the ILs still showed catalytic activity in the runs that followed, but the catalytic activity quickly decreased. Thus, a yield of 51.2% was obtained in the first run (with PCl_3:benzene:ILs (X = 2), equals to 30:15:1), and yields of 24.3% and 6.1% were obtained, respectively, in the following reactions when the ILs were reused. After the reaction, there is some yellow solid in the ropy ionic liquids residues, and unlike that in the $[Et_3NH]Cl\text{-}XAlCl_3$-catalyzed reactions, the weight of the $[Et_4N]Br\text{-}XAlCl_3$ residues did not increased.

Isolation of DCPP From the Complex DCPP·$AlCl_3$ and the Ionic Liquid Residues

In both the $[Et_3NH]Cl\text{-}XAlCl_3$ and $[Et_4N]Br\text{-}XAlCl_3$, ionic liquids catalyzed reactions of PCl_3 and benzene; the reactions could be carried out with a catalytic amount of catalyst, but the catalytic activity was

TABLE III Reusable Characters of $[Et_4N]Br\text{-}2AlCl_3$ Ils

PCl_3:benzene: ILs/mole ratio	[a]Runs	Yield/%
30:15:1	1	51.2
30:15:1	2	24.3
30:15:1	3	6.1
30:10:1	1	48.8
30:10:1	2	28.5
30:10:1	3	12.6

[a]Reactions were carried out with refluxing for 6 h.

TABLE IV Comparisons of the Coordination Properties for the Two Kinds of IL: Isolation of DCPP by Extraction the Complexes With Solvents and the Recovery of DCPP by Distillation at a Reduced Pressure

Case no.	Complex	Extraction procedure	Recovery of DCPP, %
Case 1	DCPP $AlCl_3$	Extraction with petroleum ether	0[a]
Case 2	DCPP·$AlCl_3$	Extraction with PCl_3	0[a]
Case 3	ILs + DCPP (ILs = $[Et_3NH]Cl$-$2AlCl_3$, with $AlCl_3$:DCPP molar ratio = 1:1)	Extraction with PCl_3; phase separation; then extraction the ILs phase with petroleum ether	38[a]
Case 4	ILs + DCPP (ILs = $[Et_4N]Br$-$2AlCl_3$, with $AlCl_3$:DCPP molar ratio = 1:1)	Extraction with PCl_3; phase separation; then extraction the ILs phase with petroleum ether	79[a]
Case 5	$[Et_3NH]Cl$-$2AlCl_3$ residue	Extraction after addition of $[Et_3NH]Cl$	>62[b]
Case 6	$[Et_4N]Br$-$2AlCl_3$ residue	Extraction after addition of $[Et_4N]Br$	0[b]

[a] The recovery of DCPP is calculated based on the DCPP used in the preparation of complex.

[b] The recovery of DCPP is calculated based on the weight increase of the IL residue after each reaction.

reduced as they were recycled. The reason for the reduction of the catalytic activity is complicated. Decomposition and leaching of the catalyst into the solvent phase might take place during the reaction and separation process. Nevertheless, this is not obvious, as shown by the experimental data in Table IV. In fact, the coordination property of the ionic liquid can be changed with the changing of anion. Table IV lists the comparisons of the coordination properties for the two kinds of ionic liquid. In the experimental cases 1 and 2 in Table IV, a comparison for the extraction ability of petroleum ether or PCl_3 for the DCPP from the complex $AlCl_3$·DCPP was made. The complex ($AlCl_3$·DCPP) was used for the DCPP isolation and was prepared by mixing an equal molar of DCPP with $AlCl_3$. The results, which are listed in Table IV, show that there was no DCPP that could be extracted directly. In cases 3 and 4, same amount of DCPP was added at first to the two kinds of ILs, respectively. Then, DCPP could be isolated by extracting the two kinds of complex with an equal amount of solvent and by distillation at reduced pressure. A comparison can be made for the recovery of DCPP that was calculated based on the initial amount DCPP used in the preparation of complex. From the experimental data, it is clear that the coordination of DCPP with the $[Et_3NH]Cl\text{-}XAlCl_3$ ionic liquid is stronger than the coordination of DCPP with the $[Et_4N]Br\text{-}XAlCl_3$ ionic liquid. For case 4, the DCPP recovery is 79%, while for case 3, it is only 38%. This agrees with the evidence that with the use of the new catalyst, the weight of the ILs residue was scarcely increased after the reaction.

In subsequent experiments, the reaction residues from the above two kinds of ionic liquid ($[Et_3NH]Cl\text{-}XAlCl_3$ and $[Et_4N]Br\text{-}XAlCl_3$) were treated with quaternary ammonium, respectively, to show if there exists complex $AlCl_3{\cdot}DCPP$ in them. The complex can be broken by the addition of quaternary ammonium with the following $AlCl_3$-consuming reactions:

$$[AlCl_4]^- + AlCl_3 \rightarrow [Al_2Cl_7]^- \quad (2)$$

$$AlCl_3 + [Et_3NH]Cl \rightarrow [Et_3NH]^+ + [AlCl_4]^- \quad (3)$$

$$AlCl_3 + [Et_3NH][AlCl_4]^- \rightarrow [Et_3NH]^+ + [Al_2Cl_7]^- \quad (4)$$

$$AlCl_3{\cdot}DCPP + [Et_3NH]Cl \rightarrow [Et_3NH]^+ + [AlCl_4]^- + DCPP \quad (5)$$

$$AlCl_3{\cdot}DCPP + [Et_3NH][AlCl_4]^- \rightarrow [Et_3NH]^+ + [Al_2Cl_7]^- + DCPP \quad (6)$$

Here we assume that there may exist complex $AlCl_3{\cdot}DCPP$ in the IL's catalyzed reactions, which may contribute to the weight increase of the residues and the reduction of the catalytic activity. In case 5, there was 62% DCPP isolated from the $[Et_3NH]Cl\text{-}XAlCl_3$ IL residue (the recovery of DCPP was calculated based on the weight increase of the IL residue after the Friedel-Crafts reaction). It indicated that there does exist a complex of $AlCl_3$ and DCPP in the residues, and the addition of quaternary ammonium can make the DCPP isolated. The formation of the complex of $AlCl_3$ and DCPP in the IL's residues consumed part of the $AlCl_3$, which changed its acid/base character. This may explain the results obtained from the $[Et_3NH]Cl\text{-}XAlCl_3$ catalyzed reactions, that the ionic liquids were recyclable with reduced catalytic activity.

In case 6, using $[Et_4N]Br$ as a comparison with case 5, there was no DCPP isolated from the $[Et_4N]Br\text{-}XAlCl_3$ IL's residue. This tendency agrees with the result in case 4 (the coordination of DCPP with the $[Et_4N]Br\text{-}XAlCl_3$ ionic liquid is weak, so that after extraction, there is little DCPP remaining in the residue), and it shows how the coordination property of the ILs is effected by the different anions.

In another one of our articles,[15] the IL was used to catalyze the reaction of DCPP with sulfur to produce dichloride phosphinic sulfide (DCPPS). It was found that the ILs catalyst could be recycled many times without losing activity. Thus, in this article, the remaining part of DCPP existed as a complex state in the IL's residues and reacted with sulfur at first, then, the produced DCPPS was extracted with petroleum ether. Separation for the petroleum ether phase allowed the IL catalyst to be regenerated.

CONCLUSIONS

1. The Friedel-Crafts reaction of PCl_3 and benzene was carried out in this work. Instead of using $AlCl_3$ as a catalyst, the adduct of $AlCl_3$ with ammonium salt ($[Et_4N]Br$-$XAlCl_3$ ILs) was used as a catalyst. Compared with the classical methods to prepare DCPP, the reaction using $[Et_4N]Br$-$XAlCl_3$ ILs as catalyst exhibited a simple product isolation procedure and less catalyst consumption, and the unreacted raw materials could be reusable, which will contribute to the clean synthesis of DCPP.
2. From special extraction experiments, it was found that some DCPP do exist in the $[Et_3NH]Cl$-$XAlCl_3$ residues, and to treat the reaction residue of the IL phase with $[Et_3NH]Cl$ quaternary ammonium is helpful to isolate the DCPP. Through the experiment by extraction of DCPP from the ionic liquid residue, it was shown that there is less DCPP complex with anion of $Al_2Cl_6Br^-$. The effect of the changing anion on the catalyst recycling and product isolation is obvious.
3. For the reaction catalyzed with an acidic $AlCl_3$ IL to produce DCPP, the yield that was achieved cannot reach the level with normal $AlCl_3$ as a catalyst. However, from a point of view of reactant recycling, when comparing a yield of how much moles of DCPP are produced with one mole $AlCl_3$, using ILs as a catalyst has an advantage of less catalyst consumption, and, therefore, brings out less waste.

REFERENCES

[1] L. D. Quinn, A Guide to Organophosphorus Chemistry (John Wiley and Sons, 2000).
[2] A. W. Frank, *J. Org. Chem.*, **24,** 966 (1959).
[3] G. M. Kosolapoff and W. F. Huber, *J. Am. Chem. Soc.*, **69,** 2020 (1947).
[4] B. Buchner and L. B. Lockhart, *Organic Synthesis*, **31,** 88 (1951).
[5] W. T. Dye, Jr., *J. Am. Chem. Soc.*, **79,** 2595 (1948).
[6] J. A. Boo, J. A. Levisky, J. C. Pflug, and J. S. Wilkes, *J. Org. Chem.*, **51,** 480 (1986).
[7] K. S. Yeung, M. E. Farkas, Z. Qiu, and Z. Yang, *Tetrahedron Letters*, **43,** 5793 (2002).
[8] M. H. Valkenberg, C. Decastro, and W. F. Hölderich, *Appl. Catal. A: Gen.*, **215,** 185 (2001).
[9] C. J. Adams, M. J. Earle, G. Roberts, and K. R. Seddon, *Chem. Commun.*, 2097 (1998).

[10] Z.-W. Wang and L.-S. Wang, *Green Chem.*, **5,** 737 (2003).

[11] Z.-W. Wang and L.-S. Wang, *Appl. Catal. A: Gen.*, **262,** 101 (2004).

[12] G. M. Kosolapoff, *J. Am. Chem. Soc.*, **72,** 4292 (1950).

[13] J.-S. Wu, X.-Y. Sun, and L.-S. Wang, *J. Chem. Eng. Data*, **46,** 1123 (2001).

[14] B. Buchner and L. B. Lockhart, Jr, *J. Am. Chem. Soc.*, **73,** 755 (1951).

[15] C.-G. Wang, H.-B. Kang, Z.-W. Wang, and L.-S. Wang, *J. Austr. Chem.*, accepted, 2004.