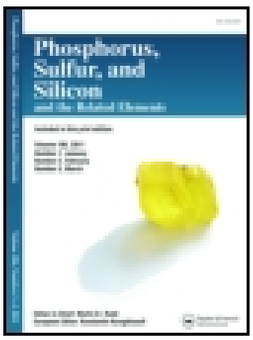

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Synthesis of *N*-Phenylphosphoramidothioic Dichloride

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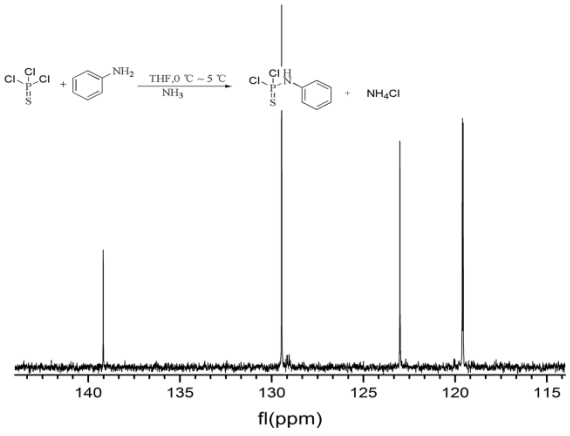
Abstract

N-Phenylphosphoramidothioic dichloride was successfully synthesized from the reaction of thiophosphoryl chloride and phenylamine. Ammonia was used as acid-binding agent in the reaction. The product was fully characterized by IR, NMR (^{1}H, ^{13}C and ^{31}P), and EA. Under the optimized conditions, the overall yield was 85%. There are many advantages for this synthesis method such as simple synthesis procedure, low cost of production, and few by-products.



Keywords

N-Phenylphosphoramidothioic dichloride; acid-binding agent; organophosphorus; thiophosphoryl chloride

ACCEPTED MANUSCRIPT

Introduction

Organophosphorus compounds have attracted considerable interest of chemists worldwide for their excellent biological activity; many phosphorylated derivatives of them were used as pesticides, insecticides, fungicides, and urease inhibitors[1] and have been widely applied in medicinal chemistry, pharmacochemistry and agriculture. The outstanding biological activity of the phosphoryl group drives our interest to further expand the scopes of phosphorylated compounds to apply to various fields.

In agriculture we always apply various synthetic nitrogen fertilizers to improve the uptake of nitrogen. But the fertilizers such as urea are easily hydrolyzed to NH_4^+ ions, which causes in the respective zones high pH and conductivity due to NH_3 volatilization.[2] The urease inhibitors such as *N*-(*n*-butyl) thiophosphorictriamide (NBPT) have shown a highly efficiency in reducing NH_3 losses from surface-applied urea and increasing the yield of nitrogen uptake.[3] A number of urease inhibitors have been reported.[4,5] *N*-Phenyl thiophosphorictriamide (NPPT) is a derivative of NBPT and the critical step for its synthesis is the preparation of *N*- phenyl phosphoramidothioic dichloride (NPPD). NPPD is also a valuable intermediate with important application in the synthesis of dichlorophosphinothioyl derivatives,[6,7] oligonucleotide phosphorodithioates,[8] and phosphorus containing flame retardants.[9,10] The synthesis of NPPD has been reported in the literature.[8,11-13] In this paper we report a synthetic route to NPPD using ammonia as acid-binding agent (Scheme 1).

Results and Discussion

The pesticide intermediate NPPD was synthesized by nucleophilic substitution reaction of thiophosphoryl chloride with phenylamine. The structure of NPPD was confirmed by FTIR (Figure 1). The stretching vibration of C---H and P---Cl was observed at 3041 cm^{-1} and 580 cm^{-1}, respectively. The peaks at 1597 and 1497 cm^{-1} were attributed to the framework vibration of the benzene ring and the absorption bands at 751 cm^{-1} and 688 cm^{-1} corresponded to the vibration of a singly substituted benzene ring. The peaks at 3250-3400 cm^{-1} can be assigned to N---H stretching[14] and the peak 1597 cm^{-1} was associated with the bending absorption mode of N---H. There is a weak absorption band at about 760-800 cm^{-1}, which may be associated with the stretching mode of P = S. Because of the effect of electronic effect of chlorine, the stretching absorption of P = S was observed higher wave numbers than that reported in the literature (580--750 cm^{-1})[6,15].

The ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of NPPD was also shown in Figure 1. The signal of the NH proton was observed at δ = 5.30 ppm and the signals of the aromatic protons were observed between 6.94 and 7.20 ppm. The $^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, $CDCl_3$) of NPPD is shown in Figure 2. The signals at δ = 119.6, 123.0 and 129.5 ppm are attributed to the *ortho*, *para* and *meta* carbon atoms of the benzene ring, respectively. The NMR signal of the *ipso* carbon atom is observed at δ = 139.2 ppm.

The purity of NPPD was also confirmed by its ^{31}P NMR (200 MHz, $CDCl_3$) spectrum illustrated in Figure 2. There was only one ^{31}P resonance observed at δ = 42.6 ppm.

Experimental

Materials

Unless otherwise noted, all reagents used (phenylamine, benzene, tetrahydrofuran, methanol, petroleum ether, ethanol, and ethyl acetate) were commercially available (Chengdu Kenong reagent Co., Chengdu, China), and were used without further purification. Thiophosphoryl chloride (97 wt %) was obtained from Chengdu Xiya reagent Co., (Chengdu, China); ammonia (99.99 vol %) was obtained from Messer gas Co..

Characterization

FTIR spectrum was recorded with a Spectrum One infrared spectrophotometer (PE, USA) using KBr pellets. ^{1}H, ^{13}C and ^{31}P NMR spectra were obtained with a Bruker Avance NMR spectrometers (Bruker, Suisse). Elemental analysis was performed with a Varian EL CUBE elemental analyzer (Elementar Analysensysteme GmbH, Germany). The melting point was determined using an Optimelt OPM100 apparatus.

Preparation of NPPD

Phenylamine was dried by refluxing with calcium hydroxide for 4-6 h and then and distilled after standing for 12 h; tetrahydrofuran was refluxed overnight with sodium and diphenylketone as tracer agent for water removing. Thiophosphoryl chloride was freshly distilled before use. A solution of 29.50 g thiophosphoryl chloride in 47.90 g of tetrahydrofuran was cooled to 0-5°C in a 500 mL three-necked round bottom flask which was set in a cryogenic cooling circulation machine (DL-4020, Ningbo Scientz biotechnology Co., Ltd, China), after the flask is flushed

with nitrogen. Then a solution of 22.70 g phenylamine in 33.60 g of tetrahydrofuran was added dropwise into the flask with constant stirring. After all of the phenylamine solution were added, the reaction mixture was kept about 2.5 h at the same temperature until a white emulsion showed up. By thin layer chromatography (TLC) we could see that the reaction of the thiophosphoryl chloride was complete. During the process, ammonia was bubbled into the system intermittently with appropriate velocity. After filtering the solvent was removed at reduced pressure and a solid was obtained. The solid was dried in vacuum and dissolved in an appropriate amount of ethyl acetate with stirring in the ultrasonic cleaning machine (SB-5200DTN, Ningbo Scientz Biotechnology co., Ltd, China); it took about 2 min to dissolve. Through lowering temperature the pure product precipitated as a white solid, which was filtered and dried (33.1 g, yield 84.7%). Elemental analysis: Calcd for NPPD: C 31.77, H 2.64, N 6.21, S 14.21%; Found: C 31.85, H 2.65, N 6.19, S 14.15%. M. p.: 41 °C.

Conclusion

In summary, we have developed a large scale synthesis of NPPD by using thiophosphoryl chloride and phenylamine. The reaction proceeds under very mild reaction conditions and NPPD can be obtained in good yield.

Acknowledgment

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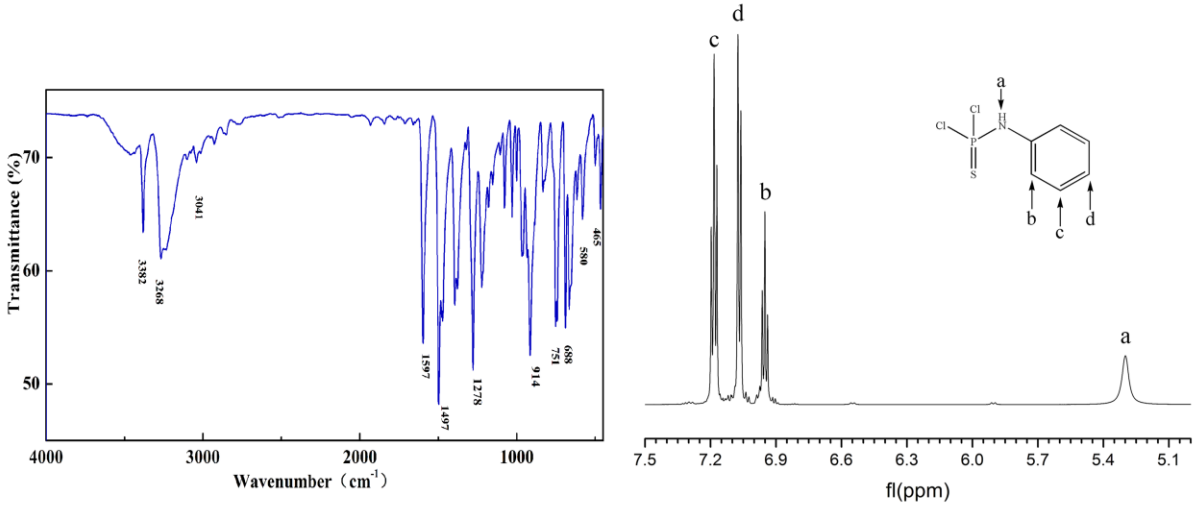


Figure 1 IR and ^{1}H NMR spectrum of NPPD

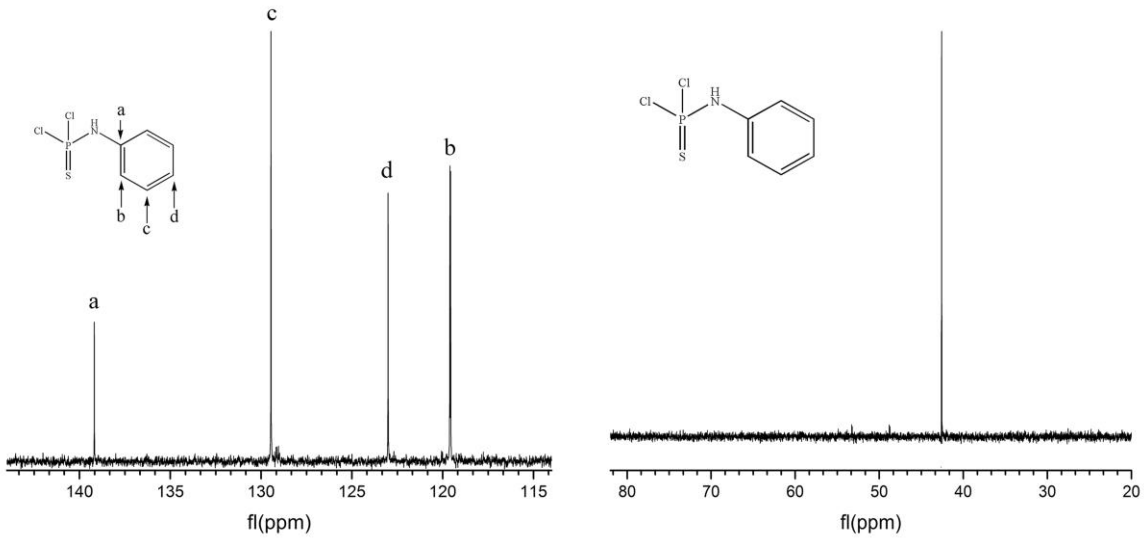
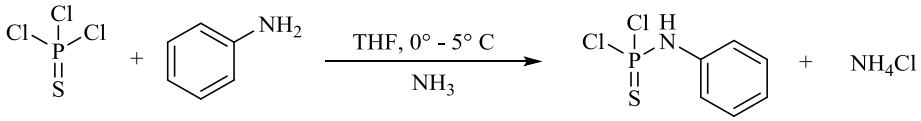


Figure 2 ^{13}C and ^{31}P NMR spectrum of NPPD



Scheme 1 Synthesis of NPPD