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Nucleophilic Catalysis of Phosphorus Trichloride Oxygen Oxidation

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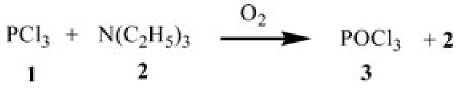
ABSTRACT: *The effect of nucleophilic catalysis on phosphorus trichloride oxygen oxidation is discovered. A number of nucleophilic catalysts for the phosphorus trichloride oxidation are found. Triethylamine, 4-dimethylaminopyridine (DMAP), and tetramethylurea are amongst them.* © 2008 Wiley Periodicals, Inc. Heteroatom Chem 19:408–411, 2008; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/hc.20439

INTRODUCTION

Phosphorus oxychloride manufacturing technology is based on the phosphorus trichloride oxidation [1]. The process is carried out by direct phosphorus trichloride oxidation with pure oxygen or with air at the temperature ranging from 60 to 700°C, often the pressure is used [2–6]. Catalysts' use enables the reaction at ambient temperature. The following catalysts were used: Lewis acids such as ferric chloride and trimethylchlorosilane [7]; variable-valence metal oxides, for example, manganese oxide (IV) [8]; radical catalysts, such as hydrogen peroxide [9]. We wish to report the first example of nucleophilic catalysis of phosphorus trichloride oxidation with oxygen.

RESULTS AND DISCUSSION

Complete oxidation of PCl_3 to $POCl_3$ easily occurs when a slow stream of dry pure oxygen is passed through a solution of PCl_3 and 3 equivalents of triethylamine in chloroform at room temperature. Gradual decrease in 220 ppm signal intensity in the ^{31}P NMR spectra, which corresponds to **1**, and synchronous increase in 3.5 ppm signal intensity, which corresponds to **3**, were observed during the reaction.



$$\underset{\mathbf{1}}{PCl_3} + \underset{\mathbf{2}}{N(C_2H_5)_3} \xrightarrow{O_2} \underset{\mathbf{3}}{POCl_3} + \mathbf{2} \quad (1)$$

Oxidation also takes place if oxygen is substituted with air, but slowly the reaction time increases from 2.5 to 4.5 h.

Air oxidation rate decreases essentially, while PCl_3-Et_3N ratio is changed from 1:3 to 1:1. In the first case, the oxidation proceeds to the extent of 90% during 4 h, and in the latter case it proceeds to the extent of 16% during 7 h. For PCl_3-Et_3N 4:1 ratio, the oxidation product is not detected even after 10 h of dry air blowing.

Complete phosphorus trichloride oxidation can be achieved in 3 h if the process is carried out with triethylamine in benzene. Triethylamine-free reaction takes 12 h for 30% oxidation.

Complete oxidation of **1** is also achieved by blowing dry air through **1** and 3 equivalents of *N*,*N*-dimethylaminopyridine (**4**) chloroform solution at ambient temperature during 4 h. The reaction

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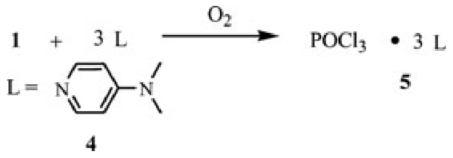
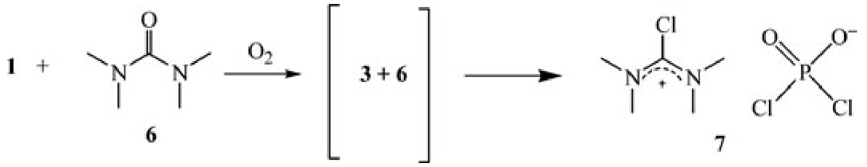
product is compound **5**, which is identical to the complex formed from $POCl_3$ and **4**.



(2)

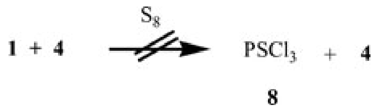
Pyridine does not have the catalytic effect in this reaction.

PCl_3 was also oxidized to **3** in the presence of tetramethylurea **6**. Immediately after formation, **3** reacts with **6** resulting in the well-known product **7** [10].



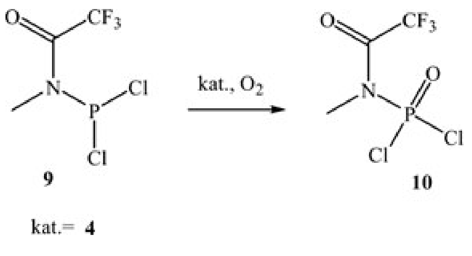
(3)

If sulfur is used as an oxidizing agent, the reaction does not occur even in the boiling solution. It is accounted for sulfur-less oxidizing ability in comparison with oxygen.



(4)

The discovered nucleophilic catalysis is also applicable to the synthesis of compound **10**, which could not be obtained by reacting **3** with *N*-methyltrifluoroacetamide. Although blowing pure oxygen through benzene solution of *N*-methyltrifluoroacetamidodichlorophosphite **9** and catalytic amount of **4** during 4 h, the oxidation of **9** is achieved resulting in *N*-methyltrifluoroacetamidodichlorophosphate **10** formation. In the absence of the catalyst, compound **9** is oxidized very slowly, and the reaction proceeds only to the extent of 5% during 4 h.



(5)

A probable catalytic mechanism supposes the formation of PCl_3 equilibrium complexes with donating ligands, leading to electron density increase at the phosphorus atom and facilitating the oxidation process. Further research on the oxidation nucleophilic catalysis is in progress.

EXPERIMENTAL

^1H and ^{31}P NMR spectra were recorded in $CDCl_3$ and $CHCl_3$ solutions on Varian VXR-300 spectrometer operating at 299.95 and 121.42 MHz, respectively. Chemical shifts (δ) are given in ppm relative to TMS as an internal standard and 85% H_3PO_4 as an external standard. Reactions were performed in water-free inert argon atmosphere. Oxidation was carried out in dried air and oxygen atmosphere; the air blowing speed reached 2 mL/s. The absence of $POCl_3$ in initial PCl_3 was strictly controlled.

Oxidation of PCl_3 with Pure Oxygen and Air Oxygen in the Presence of Triethylamine

A solution of triethylamine **2** (6.63 g, 65.5 mmol) in chloroform (2 mL) was added to a solution of PCl_3 **1** (3 g, 21.8 mmol) in chloroform (20 mL). The reaction mixture became warm, and some small crystals were formed. In ^{31}P NMR spectrum of a chilled reaction mixture, only a signal of initial **1** was observed. Dry air (or dry pure oxygen) was blown through the solution during 4.5 h (2.5 h for oxygen); the reaction was controlled by the increase in a signal, referring to phosphorus oxychloride **3** in ^{31}P NMR spectra. **1**:**3** ratio was 0.83:1 after 1 h and 0.12:1 after 4 h. NMR ($CHCl_3$): ^{31}P, δ (ppm) = 219.7 s (PCl_3), 3.7 s ($POCl_3$).

The reaction with the PCl_3-Et_3N 1:3 ratio in benzene was provided similarly. Complete oxidation of starting **1** was achieved in 3 h.

The results of PCl_3 oxidation provided in pentane and methylene chloride are similar to the abovementioned results.

After blowing dry air through chloroform solution (12 mL) of **1** (7.78 g, 56.65 mmol) and **2** (5.73 g, 56.65 mmol) during 7 h, 16% of **3** was observed in the reaction mixture. NMR ($CHCl_3$): ^{31}P, δ (ppm) = 219.7 s (PCl_3), 3.7 s ($POCl_3$).

The procedure described above was carried out for a solution of **2** (22.1 g, 218.4 mmol) and **1** (10 g, 72.8 mmol) in chloroform (60 mL). Dry air was blown through the solution during 8 h; the reaction was controlled by ^{31}P NMR spectroscopy. Then the solution was saturated with dry hydrogen chloride, 60 mL of pentane was added, and obtained crystals of triethylamine hydrochloride were filtered. The product was obtained by distillation of filtrate under normal conditions. (5.6 g; 50%). bp = 105°C. NMR ($CHCl_3$): ^{31}P, δ (ppm) = 3.7 s.

Oxidation of PCl_3 with Air Oxygen in the Presence of 4-Dimethylaminopyridine

A solution of **1** (1.12 g, 8.1 mmol) in chloroform (5 mL) was added to a solution of 4-dimethylaminopyridine **4** (2.96 g; 24.3 mmol) in chloroform (20 mL). After 30 min, a signal at 89 ppm (complex $PCl_3 \cdot x$DMAP) was observed in the solution probe spectrum. Dry air was blown through the solution during 4 h; the reaction was controlled by ^{31}P NMR spectroscopy. The increase in the signal in the spectra is attributed to the product of the reaction. Its chemical shift corresponded to the chemical shift of $POCl_3$ and *N,N*-dimethylaminopyridine **5** complex compound. Complete oxidation of initial **1** was achieved in 4 h. NMR ($CHCl_3$): ^{31}P, δ (ppm) = 89 s, (complex $PCl_3 \cdot x$DMAP), 15 s, complex ($POCl_3 \cdot 3$DMAP).

$POCl_3$ and DMAP Complex Formation

A solution of **3** (1.26 g, 8.18 mmol) in chloroform (2 mL) was added to a solution of **4** (3 g, 24.6 mmol) in chloroform (18 mL). According to ^{31}P NMR spectra, the mixture of $POCl_3$: *n*DMAP complexes (where $n = 1,2,3$) with the predominance of the last (signal corresponds to 15.5 ppm) was formed. In 17 days, the solution was concentrated and formed crystals were filtered. Thus, the complex of $POCI_3$ with DMAP **5** of 1:3 composition (2.5 g, 59%) was obtained. Elemental analysis calcd. (%) for $C_{21}H_{30}Cl_3N_6OP$ (519,83): C 48.52, H 5.82, Cl 20.46, N 16.17, P 5.96; Found C 45.31, H 5.45, Cl 18.31, N 14.62, P 5.97. NMR: ^1H ($CDCl_3$), δ (ppm) = 3.20s (18H, N-CH_3), 6.79d (6H, CH (β-arom.) ($J_{HH} = 7$ Hz)), 8.26d (6H, CH (α-arom.) ($J_{HH} = 7$ Hz)), ^{31}P ($CHCl_3$), δ (ppm) = 15.5 s.

Oxidation of PCl_3 with Air Oxygen in the Presence of N,N,N′,N′-Tetramethylurea

A solution of **1** (1.182 g, 8.6 mmol) in chloroform (5 mL) was added to a solution of tetramethylurea **6** (3 g, 24.6 mmol) in chloroform (20 mL). In 30 min, a signal at 219 ppm, which corresponds to initial **1**, was observed in the solution probe spectrum. Dry air was blown through the solution during 5 h, and the reaction was controlled by ^{31}P NMR spectroscopy. The increase in the signal in the spectra is attributed to the product of the reaction. Its chemical shift corresponded to the chemical shift of the reaction product of $POCl_3$ with tetramethylurea **7**. Complete oxidation of initial **1** was achieved in 5 h. NMR ($CHCl_3$): ^{31}P, δ (ppm): −5.8 s, (tetramethylchloroformamidinium dichlorophosphate **7**).

*Reaction of $POCl_3$ with N,N,N′,N′-Tetramethylurea; Synthesis of Tetramethylchloroformamidinium Dichlorophosphate (**7**)*

A solution of **3** (1.32 g, 8.6 mmol) in chloroform (5 mL) was added to a solution of tetramethylurea **6** (1 g, 8.6 mmol) in chloroform (20 mL). According to ^{31}P NMR spectroscopy data, the initial compounds were gradually converted into the product **7**. After 6 days, the solvent was evaporated, and 20 mL of diethyl ether was added to the obtained oil. Obtained crystals were filtered and washed with diethyl ether (2.0 g, 86%). Elemental analysis calcd (%) for $C_5H_{12}Cl_3N_2O_2P$ (269.5): C 22.28, H 4.49, Cl 39.47, N 10.39, P 11; Found C 22.17, H 4.36, CI 39.34, N 10.38, P 10.99. NMR: ^1H ($CDCl_3$), δ (ppm) = 3.49 s (12H, N-CH_3), ^{31}P ($CHCl_3$), δ (ppm) = −5.60 s.

*N-Methyl-N-trifluoroacetamidodichlorophosphate (**10**)*

Eighty milligrams (0.66 mmol) of **4** was added to a solution of 25.7 g (0.113 mol) *N*-methyl-*N*-trifluoroacetamidodichlorophosphite **9** in benzene (10 mL), and pure dry oxygen was blown through the solution during 4 h. After the reaction mixture vacuum distillation, *N*-methyl-*N*-trifluoroacetamidodichlorophosphate **10** was obtained, and its physicochemical properties are identical to the product obtained earlier [11] (16.5 g, 60%). bp 70–72°C (10 Torr). NMR ($CDCl_3$): ^{31}P, δ (ppm) = 10.3 q ($^3J_{PH} = 11.0$ Hz), ^{19}F, δ (ppm): −71.0 s.

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