Phenyl Dichlorophosphate –
A Versatile Reagent

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Introduction

Among several phosphorus acid chlorides described for use in organic synthesis, phenyl dichlorophosphate (PDCP, 1) has received added interest due to its powerful phosphorylating nature. The activity of PDCP compared to other chlorophosphate esters was shown to be superior. Phenyl dichlorophosphate is regarded as the most widely used reagent for the preparation of symmetrical phosphate diesters.1 Other important PDCP-derived phosphorylating agents, e.g. phenylphosphoro di-(1-imidazolidate), 2-phenylbis-triazoloylphosphate have been used in peptide synthesis.2

Phenyl dichlorophosphate (1) is conveniently prepared by reaction of phosphorus oxychloride with anhydrous powdered sodium phenoxide.3 The precipitated sodium chloride is filtered off and excess phosphorus oxychloride is removed under reduced pressure. The crude oil is distilled in a vigreux column and the fraction having the boiling point 103-106 °C (9 mmHg) is collected for chemical reactions.

Abstracts

(A) PDCP acts as an activating agent for the formation of thiol esters in good yield by the condensation of carboxylic acids and thiols in the presence of pyridine. Other chlorophosphates such as (PhO)2P(O)Cl and (EtO)2P(O)Cl have proven to be less efficient for the direct transformation of carboxylic acid to thiol ester.4

(B) PDCP has been used for the halogenation of β-diketones. Conversion of β-diketones to the corresponding β-chloro-α,β-unsaturated ketones is activated by PDCP in the presence of a base, generally lithium hydride.5a A combination of PDCP and DMSO in methylene chloride provides immediate access to the intermediates of carvone and limonene derivatives by a facile rearrangements of pinenes.5b

(C) PDCP has been shown to be an efficient DMSO-activating agent in the Pfizner-Moffatt oxidation. It is conceivable that a complex salt ([PhOPOC13OS+(CH3)2]Cl–), generated from the PDCP and DMSO, serves as an oxidizing agent for the conversion of primary and secondary alcohols to the corresponding aldehydes and ketones.6

(D) PDCP and DMSO can be used in the oxidative deamination process for benzyl amines to the corresponding carbonyl compounds.7

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