

SYNLETT Spotlight 380

Phosphoric Trichloride

Compiled by Haibao Duan

This feature focuses on a reagent chosen by a postgraduate, highlighting the uses and preparation of the reagent in current research

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Introduction

Phosphoric trichloride is a colorless, clear and transparent irritating liquid. Its structure is a tetrahedral consisting of one P=O double bond and three P–Cl bonds. POCl₃ reacts with alcohols to produce alkyl phosphate esters and is therefore a versatile phosphoryating agent.¹ As a selective and inexpensive reagent giving high yields in simple operations under mild conditions, it is tremendously used in

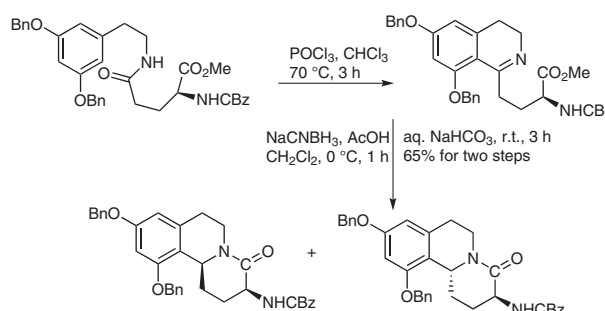
organic synthesis, for example, in chlorination,² regioselective dehydration and ring-closing reactions.³ Its use has been reported in several types of name reactions, for example, in the Bischler–Napieralski⁴ and Vilsmeier–Haack reactions.⁵



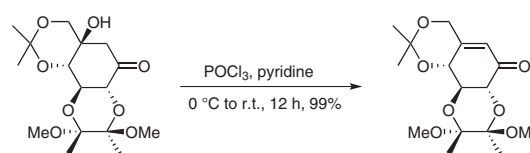
Figure 1 Phosphoric trichloride

Abstracts

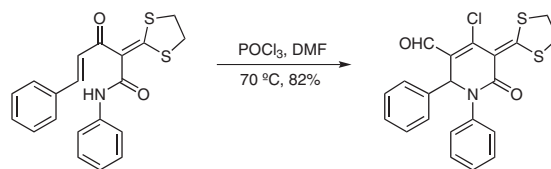
(A) The Bischler–Napieralski reaction has been widely used to prepare feature heterocycles of numerous natural products and related compounds. In the total syntheses of schulzeines B and C, Gurjar and co-workers employed POCl₃ for the formation of isoquinoline.⁶



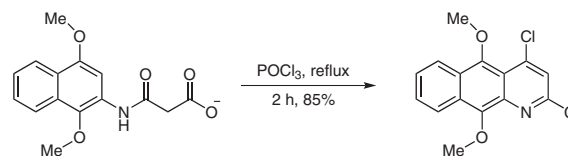
(B) Shing and co-workers have described the mild quantitative regioselective elimination of the tertiary alcohol with POCl₃ affording the enone.⁷



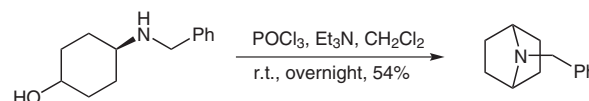
(C) The Vilsmeier reagent (DMF/POCl₃) was used to efficiently and directly synthesize polyfunctionalized unsaturated δ -lactams⁸ via cyclization–haloformylation.



(D) Groth and co-worker reported the total syntheses of kalasinamide, geovamine and marcanine A.⁹ During the second key step, after optimization, the yield of cyclization and chlorination of a malonic acid amide in presence of POCl₃ is 85%.



(E) The title reagent and triethylamine can convert commercially available *trans*-4-aminocyclohexanol to the corresponding cyclodehydration product in 54% yield under mild conditions.¹⁰



References

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