

# 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

Haibao Duan was born in Henan Province, P. R. of China. He received a M.Sc. in fine chemistry from Jiangnan University (Wuxi, P. R. of China) in 2004 and is now working towards his Ph.D. in organic chemistry under the supervision of Prof. Guomin Xiao at the School of Chemistry and Chemical Engineering in Southeast University. His research is focused on the development of new methods for the synthesis of novel photoinitiators.

School of Chemistry and Chemical Engineering, Southeast University, Nanjing 211189, P. R. of China  
E-mail: duan4588@163.com



### 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. POCl<sub>3</sub> reacts with alcohols to produce alkyl phosphate esters and is therefore a versatile phosphoryating agent.<sup>1</sup> As a selective and inexpensive reagent giving high yields in simple operations under mild conditions, it is tremendously used in

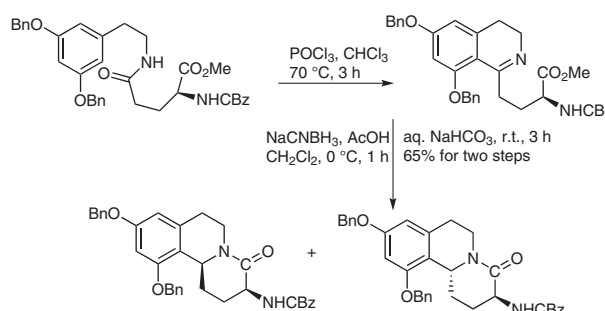
organic synthesis, for example, in chlorination,<sup>2</sup> regioselective dehydration and ring-closing reactions.<sup>3</sup> Its use has been reported in several types of name reactions, for example, in the Bischler–Napieralski<sup>4</sup> and Vilsmeier–Haack reactions.<sup>5</sup>



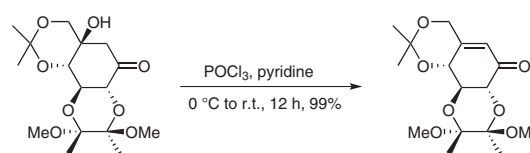
Figure 1 Phosphoric trichloride

### Abstracts

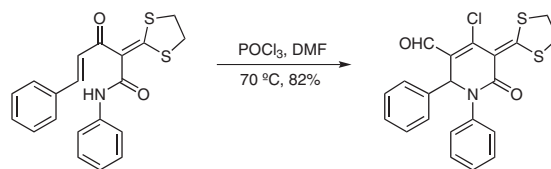
(A) The Bischler–Napieralski reaction has been widely used to prepare feature heterocycles of numerous natural products and related compounds. In the total syntheses of schulzeines B and C, Gurjar and co-workers employed POCl<sub>3</sub> for the formation of isoquinoline.<sup>6</sup>



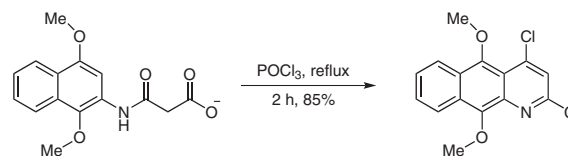
(B) Shing and co-workers have described the mild quantitative regioselective elimination of the tertiary alcohol with POCl<sub>3</sub> affording the enone.<sup>7</sup>



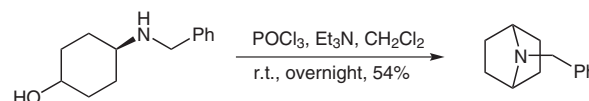
(C) The Vilsmeier reagent (DMF/POCl<sub>3</sub>) was used to efficiently and directly synthesize polyfunctionalized unsaturated  $\delta$ -lactams<sup>8</sup> via cyclization–haloformylation.



(D) Groth and co-worker reported the total syntheses of kalasinamide, geovamine and marcanine A.<sup>9</sup> During the second key step, after optimization, the yield of cyclization and chlorination of a malonic acid amide in presence of POCl<sub>3</sub> 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 condition.<sup>10</sup>



## References

- (1) Muramatsu, N.; Takenish, T. *J. Org. Chem.* **1965**, *30*, 3211.
- (2) Robiins, R. K.; Christensen, B. E. *J. Am. Chem. Soc.* **1952**, *74*, 3624.
- (3) Meth-Cohn, O.; Rhouati, S.; Tarnowski, B.; Bobinson, A. *J. Chem. Soc., Perkin Trans. 1* **1981**, 1537.
- (4) Fodor, G.; Gal, J.; Phillips, B. A. *Angew. Chem. Int. Ed.* **1972**, *11*, 919.
- (5) Alunni, S.; Linda, P.; Marino, G.; Santini, S.; Savelli, G. *J. Chem. Soc., Perkin Trans. 2* **1972**, 2070.
- (6) Gurjar, M. K.; Pramanik, V.; Bhattasali, D.; Ramana, C. V.; Mohapatra, D. K. *J. Org. Chem.* **2007**, *72*, 6591.
- (7) Shing, T. K. M.; Cheng, H. M.; Wong, W. F.; Kwong, C. S. K.; Li, J. M.; Lau, C. B. S.; Leung, P. S.; Cheng, C. H. K. *Org. Lett.* **2008**, *10*, 3146.
- (8) Liu, J.; Wang, M.; Han, F.; Liu, Y. Y.; Liu, Q. *J. Org. Chem.* **2009**, *74*, 5090.
- (9) Lang, S.; Groth, U. *Angew. Chem. Int. Ed.* **2009**, *48*, 911.
- (10) Pérez, M.; Contelles, J. M. *Synthesis* **2009**, 3649.