SYNLETT Spotlight 380

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

Phosphoric Trichloride

Compiled by Haibao Duan

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. POCl₃ reacts with alcohols to produce alkyl phosphate esters and is therefore a versatile phosphating 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 regiospecific 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

BnO

'nΒr

aq. NaHCO₃, r.t., 3 h 65% for two steps

CO₂Me

NHCB2

NHCBz

POCI₃, CHCl₃

70 °C, 3 h

NaCNBH₃, AcOH CH₂Cl₂, 0 °C, 1 h

BnC

BnO

BnC

Figure 1 Phosphoric trichloride

CO₂Me

ÓВг

NHCBz

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 regiospecific elimination of the tertiary alcohol with $POCl_3$ affording the enone.⁷

SYNLETT 2012, 23, 319–320 Advanced online publication: 04.01.2012 DOI: 10.1055/s-0031-1290126; Art ID: V38711ST © Georg Thieme Verlag Stuttgart · New York





NHCB2

(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 converse commercially available *trans*-4-aminocyclohexanol to the corresponding cyclode-hydration product in 54% yield under mild condition.¹⁰



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.