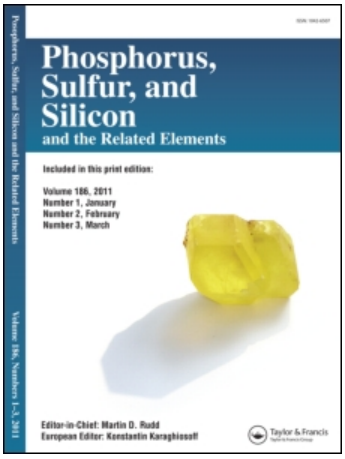


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Fluorinated Organophosphorus Compounds as a New Class of Agrochemicals

Chengye Yuan; Weisheng Huang; Shoujun Chen; Yixin Zhang

To cite this Article Yuan, Chengye , Huang, Weisheng , Chen, Shoujun and Zhang, Yixin(1999) 'Fluorinated Organophosphorus Compounds as a New Class of Agrochemicals', Phosphorus, Sulfur, and Silicon and the Related Elements, 144: 1, 625 — 628
To link to this Article: DOI: 10.1080/10426509908546322
URL: http://dx.doi.org/10.1080/10426509908546322

Phosphorus, Sulfur and Silicon, 1999, Vol. 144-146, pp. 625-628
Reprints available directly from the publisher
Photocopying permitted by license only

Fluorinated Organophosphorus Compounds as a New Class of Agrochemicals

CHENGYE YUAN, WEISHENG HUANG, SHOUJUN CHEN and YIXIN ZHANG

Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 354 Feng Lin Lu, Shanghai 200032, CHINA

New methods for the synthesis of fluorinated aminophosphonic acids and phosphonopeptides are described. Some structural effects on bioactivity of trifluoromethylimidazole is discussed.

Keywords: fluorinated aminophosphonic acids; trifluoromethylimidazole

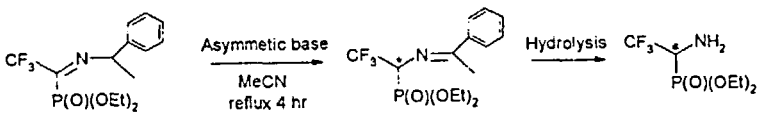
INTRODUCTION

The increasing and sustained interest in aminophosphonic acids and derivatives thereof has had an explosive impact on the design and synthesis of functionalized aminophosphonic acids. Introduction of a fluorine atom into a biologically active compound usually results, as a rule, in an enhancement of the parent molecule. Flynn et al[1] described the synthesis of β-fluorinated aminophosphonic acids, namely β-monofluorinated, β-difluorinated, β-trifluorinated α-aminophosphonic acids and showed the inhibitory action as alanine racemace. Gruss and Hagele[2], on the other hand, reported a general method leading to nuclear fluorinated N-phenyl phenylglycine and demonstrated that (N-p-trifluoromethoxyphenyl) phenylglycine possesses remarkable insecticidal activity toward harmful and parasitic insects. Recently, Green, Gruss, Hagele, Hudson and others reported the synthesis of a series of α-aminoarylmethylphosphonic acids with a range of fluoro, fluoroalkyl or fluoroalkoxyl substituents in the benzene ring.[3] Hass and Hagele reported an interesting reaction by which fluorinated hydroxyphosphonic esters and fluorinated N-(phenylamino)phosphonic acid ester can be formed conveniently from corresponding fluorinated aldehyde generated in situ.[4] In our laboratory, we have previously introduced a method for the synthesis of 3-amino-2-hydroxy-1,1-difluoroalkylphosphonic acid.[5] Several synthetic methods for the preparation of α-(N-substituted amino)- and β-(N-substituted amino)-2,2,2 trifluoroethylphosphonates were also introduced by us.[6,7] Zhu and his colleagues demonstrated the synthesis of perfluoroalkanesulfonyamino

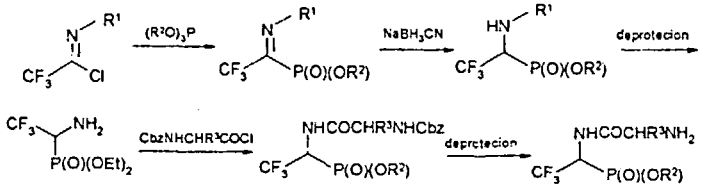
alkylphosphonic acids[8] and α-(N-pentafluorophenylamino)benzyl phosphonic acids and esters[9] by addition of diethylphosphite to corresponding aldimines followed by subsequent hydrolysis.

RESULTS AND DISCUSSION

For the preparation of chiral aminophosphonic acids we studied extensively the induced asymmetric addition of dialkylphosphite to a chiral aldimine including influence of structure of substract, catalysis as well as nature of solvents on the de value of the reaction.[10,11] The molecular mechanics calculation was also introduced by us to study the stereochemistry involed in this reaction.[12]. We report in this paper our preliminary trial on the synthesis of chiral trifluoromethylaminophosphonic acids:



The base-catalyzed [1,3] proton shift in azaallylic system of appropriate imines is widely used for the formation of a chiral carbon.[13-14] We use Cinchonine or Ephedrine as asymmetric base to induce the formation of optically active trifluoromethyl aminomethanphosphonate.[15]. Phosphonopeptides comprise a group of organophosphorus compounds with biological significance. As far as we are aware, trifluoromethylated phosphonpeptides were described only very recently.[16]



Unfortunately, by this scheme we are not able to get N-protected trifluoromethyl 1-aminophosphonates, sine N-carbobenzoxy trifluoroacetimi-

doyl chloride did not give normal Arbuzov or Pudovik reaction product with trialkylphosphite or dialkylphosphite even under high temperature (100°C) and prolong heating (48h) due to the low reactivity of the former. In order to form a peptide linkage through the N-terminal, presence of a free amino group is essential. In our modification, $NaBH_3CN$ was used to hydrogenate the C=N bond followed by subsequent remal of the N-protecting group via hydrogenolysis with palladium black or oxidative cleavage of p-methoxyphenyl moiety by CAN treatment. The manipulation of these reactions is heavy and complicate, each step requires purification with column chromatography on silica gel. As found by us, N-(α-methylbenzyl)-2,2,2-trifluoroacetimidoyl chloride underwent Arbuzov reaction smoothly with trialkylphosphite at 90°C for 40h without solvent The thermo-rearrangement product afforded upon hydrolysis at pH 2 in a mixed solvents consisting of $THF:EtOH:H_2O(1:1:2)$.

Heterocyclics are interesting compounds with significant bio-activities. Three types of imidazole derivatives namely 1-substituted-4-phosphoryl-5-trifluoromethylimidazoles, 1-substituted-4-ethoxycarbonyl-5-trifluoromethylimidazoles and 1-substituted-4-phosphorylimidazoles were synthesized and investigated as agrochemicals. Imidazoles with trifluoromethyl moiety possess significant higher activity over those molecules without trifluoromethyl group. In the meantime, phosphorylimidazoles are much strong than corresponding ethoxycarbonylimidazole in vitro testa as insecticide, fungacide, plant activitor and endoparaslicide.

Acknowledgments

The project was supported by National Natural Science Foundation of China.

References

[1] G.A. Flynn, D.W. Beight, E.H.W. Bohme, B.M. Metealf Tetrahedron Lett. **26,** 285 (1985).
[2] U. Gruss, G. Hagele Phosphorus, Sulfur and Silicon **97,** 209 (1994).
[3] D.St.C. Green, U. Gruss, G. Hagele, H.R. Hudson, L. Lindblom, M. Pianka Phosphorus, Sulfur and Silicon **113,** 179 (1996).
[4] A.M. Hass, G. Hagele J.Fluorine Chem. **78,** 75 (1996).
[5] S. Chen, C.Y. Yuan Phosphorus, Sulfur and Silicon **82,** 73 (1993).
[6] W.S. Huang, C.Y. Yuan Phosphorus, Sulfur and Silicon **106,** 163, (1995).
[7] W.S. Huang, Y.X. Zhang, C.Y. Yuan Phosphorus, Sulfur and Silicon **107,** 21, (1995).
[8] S.Z. Zhu, B. Xu, J. Zhang, C.Y. Qin, Q. Huang, C. Qu Phosphorus, Sulfur and Silicon **112,** 219, (1996).
[9] S.Z. Zhu, X.L. Jin J. Fluorine Chem. **72,** 19, (1995).
[10] C.Y. Yuan, S.H. Cui Phosphorus, Sulfur and Silicon **55,** 159, (1991).
[11] S.S. Li, G.Q. Wang, C.Y. Yuan Acta Chimica Sinica **51,** 713, (1993).
[12] C.Y. Yuan, S.S. Li, G.Q. Wang, Y.L. Ma Phosphorus, Sulfur and Silicon **81,** 27, (1993).
[13] V.S. Parmar, K.S. Bisht J. Org. Chem. **61,** 1223, (1996).

[14] T. Ono, V.P. Kukhar, V.A. Soloshonok J. Org. Chem. **61,** 6563 (1996).
[15] C.Y. Yuan, Y.X. Zhang Unpublished result.
[16] C.Y. Yuan, Y.X. Zhang, W.C. Luo, Z.P. Yao Heteroatom Chem. **9,** 139 (1998).
[17] W.S. Huang, C.Y. Yuan J. Fluorine Chem. **74,** 279, (1995).
[18] W.S. Huang, C.Y. Yuan Synthesis 1996, 511.
[19] C.Y. Yuan, W.S. Huang, Y.X. Zhang Phosphorus, Sulfur and Silicon **115,** 105 (1996).