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α -Iminotrifluoroethyl Phosphonates: The First Representatives of C-Phosphorylated N-H Imines

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α -Iminotrifluoroethyl Phosphonates: The First Representatives of C-Phosphorylated N-H Imines

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A convenient synthetic approach for previously unknown N-H imidoylphosphonates, based on addition of dialkyl phosphites to trifluoroacetonitrile, was developed. Synthetic potentialities of imines 1 existing as equilibrium mixture of E/Z isomers, were demonstrated.

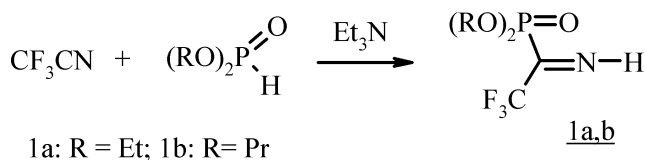
Keywords Iminoalkyl phosphonates; N-H imines; trifluoromethyl; aminophosphates

INTRODUCTION

C-phosphorylated imines are new valuable building blocks for the synthesis of various functionalized aminophosphonic acid derivatives. Compounds with trifluoromethyl group are of particular interest when specific influence of CF_3 group on the chemical and biological properties of the compounds is taken into consideration. At the same time, imidoylphosphonates with a *free* N-H group were unknown so far although they were postulated as intermediates.

RESULTS AND DISCUSSIONS

The convenient approach to imines **1**—the first representatives of previously unknown N-H iminoalkylphosphonic acid derivatives was elaborated (Scheme 1).

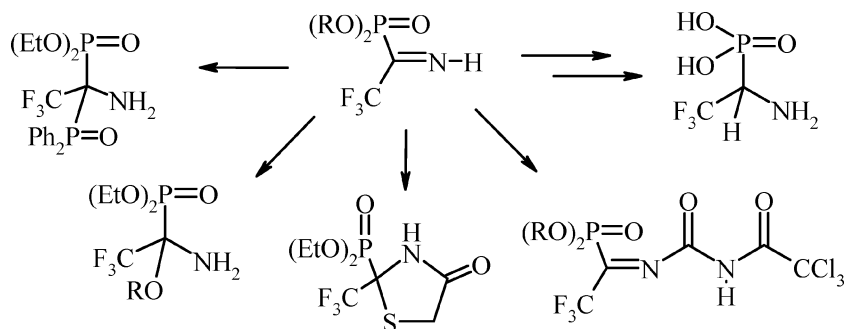


SCHEME 1

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With a few exceptions, N-H imines have been reported as unstable compounds, leading to difficulties in their isolation¹. Phosphorylated N-H imines **1** are quite stable at ordinary conditions and exist as *Z/E* mixture of stereoisomers; *Z* isomer (R = Et): δ_P -1.4 ppm, $^3J_{HP}$ 37.2 Hz, δ_F -69.7 ppm, $^3J_{FP}$ 1.9 Hz, $^4J_{FH}$ 1.2 Hz; *E* isomer: δ_P 0.7 ppm, $^3J_{HP}$ 58.2 Hz, δ_F -72.4 ppm, $^3J_{FP}$ 1.5 Hz, $^4J_{FH}$ 0.6 Hz (*Z/E* = 10:1). Obviously *Z*-isomer is stabilized by intramolecular P=O...H-bonding. Synthetic potentiality of imines **1** was demonstrated by their easy reduction and functionalization with O- and P-centered nucleophiles to afford derivatives of α -aminophosphonic acids containing



SCHEME 2

trifluoromethyl group, while interaction with mercaptoacetic acid proceeds with intramolecular cyclization of the intermediate adduct to produce the novel 2-phosphorylated N-H thiazolidone (Scheme 2). Interaction between **1** and trichloroacetyl isocyanate leads to novel reactive phosphorylated N-acylated imines.

REFERENCE

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