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PII: S0040-4039(14)01158-7
DOI: http://dx.doi.org/10.1016/j.tetlet.2014.07.017
Reference: TETL 44860

To appear in: *Tetrahedron Letters*

Received Date: 19 May 2014
Revised Date: 11 June 2014
Accepted Date: 3 July 2014

Please cite this article as: Rassukana, Y.V., Yelenich, I.P., Bezdudny, A.V., Mironov, V.F., Onys'ko, P.P., Chemoselectivity of the reactions of haloacetonitriles with hydrogen phosphonates: the dramatic effect of the nature of the halogen atom, *Tetrahedron Letters* (2014), doi: http://dx.doi.org/10.1016/j.tetlet.2014.07.017

Chemoselectivity of the reactions of haloacetonitriles with hydrogen phosphonates: the dramatic effect of the nature of the halogen atom

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Abstract Perfluoro(chloro) acetonitriles react with $(RO)_2POH$ (R = Et, Ph) by two competitive routes: addition to the C≡N bond affording the respective N-unprotected iminophosphonates, or reductive dehalogenation leading to chloro(fluoro) acetonitriles and the respective halogenophosphates, $(RO)_2P(O)X$ (X = Cl, F). The direction and chemoselectivity of the reactions are controlled by the nature and quantity of halogen atoms in the starting nitrile.

Keywords NH-iminophosphonates, nitriles, hydrophosphoryl compounds, chloro(fluoro)alkyl, addition, reduction

Addition of hydrophosphoryl compounds (HPCs) to electrophilic unsaturated substrates is a very interesting reaction in phosphorus chemistry, both in theoretical and practical aspects.[1] Reactions of HPCs with nitriles are complicated by the fact that the primary addition, as a rule, is accompanied by subsequent reaction of the initially formed and more reactive N-H iminophosphonates with the second molecule of HPC. Thus, sodium salts of dialkyl phosphites react with nitriles to yield phosphorylamino phosphonates **I**.[2a] In the presence of acids[1b,2b] or under free radical conditions,[2c] aminobisphosphonates **II**, as the main products, were reported to form in low to moderate yields (Scheme 1).

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