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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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