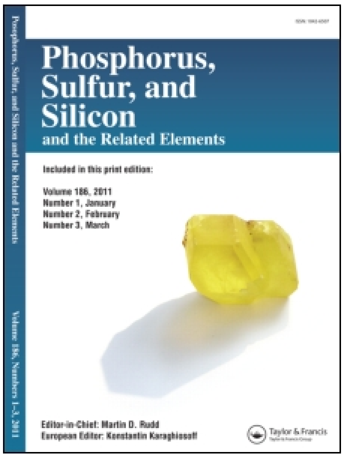

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Mono and Bisphosphonates from Perfluoro Olefins and Polyfunctional Fluoro Ketones. Syntheses, Molecular Structure and Derivatives

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Perfluoroalkenyl phosphonates were formed along with Me_3SiF using $CF_3CF=CF_2$, $CF_3CH=CF_2$, $F_5SCF=CF_2$ or $F_5SCH=CF_2$ and silylated phosphites, $(R^1O)_2POSiMe_3$ (R^1 = Et, $SiMe_3$). This straightforward method could be extended to perfluorobutadienes $CF_2=C(R^F)C(R^F)=CF_2$ (R^F F = F, CF_3). The formation of $CF_3C(=O)P(=O)(OSiMe_3)_2$ and further reactions to yield bisphosphonates will be described. Acetylphosphonates, $R^2C(=O)P(=O)(OSiMe_3)_2$ (R^2= CH_3, CF_3) reacted with the ketimine, $CH_3C(=N\mathit{i}Pr)Ph$ to give α-hydroxy-γ-imino phosphonates. Trifluoroacetylphenol and 2,6-bis(trifluoracetyl)-4-methyl-phenol have been proven to be versatile precursors for α-and γ-hydroxy phosphonates. Intermediates in these reactions were found to be cyclic $\lambda^5\sigma^5P$ species.

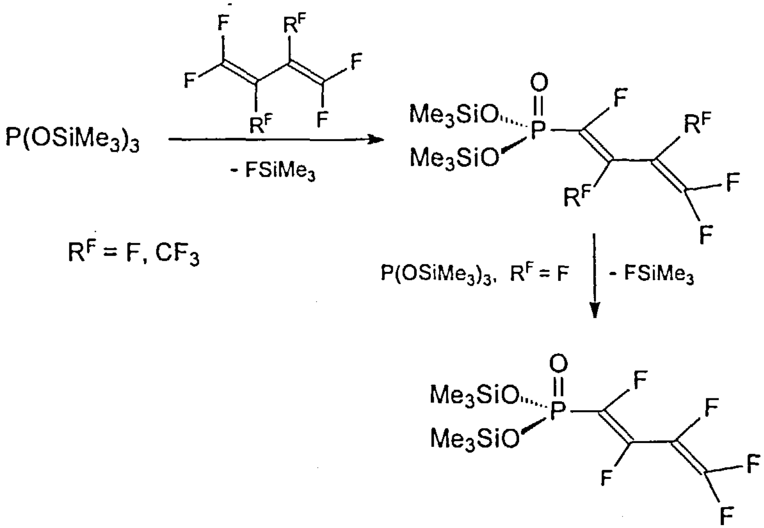
Keywords: Perfluorinated alkenes; trimethylsilylated phosphites; perfluoroalkenyl phosphonates; bisphosphonates; acetylphosphonates; 2,6-bis(trifluoroacetyl)-4-methylphenol; 1,3,2$\lambda^5\sigma^5$-dioxaphospholenes; α-,γ-hydroxy phosphonates

INTRODUCTION

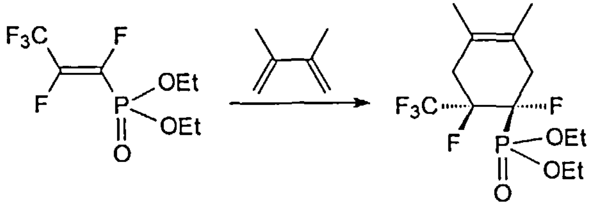
The introduction of fluorine or perfluoroalkyl groups into molecules is a versatile tool for modifying their physicochemical properties and physiological behavior. Fluorinated phosphonic acids could be considered potential fuel cell electrolytes, fluorinated bisphosphonates possible bioactive compounds. The fluorinated olefines, $R^FCF=CF_2$ and $R^FCH=CF_2$ (R^F = CF_3, SF_5) and silylated phosphites reacted to give fluorinated alkenyl phosphontes and trimethylfluorosilane in a straightforward reaction. [1a - c] Epoxides of perfluorinated olefins, e.g. of $C_6F_5(CF_3)C=CF_2$ rendered an alkenylphosphonate and two isomeric bisphosphonates. [1d]

RESULTS AND DISCUSSION

Perfluorinated dienes, $CF_2=C(R^F)C(R^F)=CF_2$ (R^F = F, CF_3) and $(Me_3SiO)_3P$ furnished either a mono (R^F = CF_3) or a bisphosphonate (R^F = F). (see Scheme 1) The analogous amido phosphonates were obtained using diamido phosphites; here, fluorophosphorane intermediate compounds were observed. Reactions could be performed at the double bond. (see Scheme 2) Acetyl phosphonates, $R^2C(=O)P(=O)(OSiMe_3)_2$ (R^2 = CH_3, CF_3) were easily prepared and could be reacted further with $(Me_3SiO)_3P$ to yield bisphosphonates, which after hydrolysis were transformed into the respective free acids. [5] However, the compounds $R^2C(=O)P(=O)(OSiMe_3)_2$ (R^2 = CH_3, CF_3) were considered analogues of CH_3COCF_3 and CF_3COCF_3 taking the electron-withdrawing capability of the $(R^1O)_2P(=O)$ group into account, [2] therefore, ketimines in their enamine tautomeric formed addition products. (see Scheme 3)

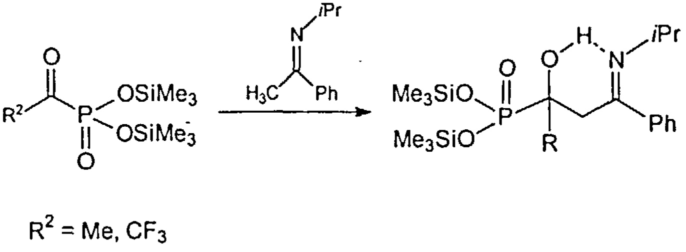


Scheme 1

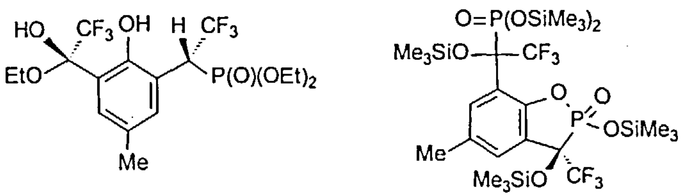


Scheme 2

2-Trifluoroacetylphenol and 2,6-bis(trifluoracetyl)-4-methyl-phenol have been proven to be versatile precursors for α- and γ-hydroxy phosphonates. (e.g. see Scheme 4)



Scheme 3



Scheme 4

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