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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 Me₃SiF using CF₃CF=CF₂, CF₃CH=CF₂, F₅SCF=CF₂ or F₅SCH=CF₂ and silylated phosphites, (R¹O)₂POSiMe₃ (R¹ = Et, SiMe₃). This straightforward method could be extended to perfluorobutadienes CF₂=C(R^F)C(R^F)=CF₂ (R^F F = F, CF₃). The formation of CF₃C(=O)P(=O)(OSiMe₃)₂ and further reactions to yield bisphosphonates will be described. Acetylphosphonates, R²C(=O)P(=O)(OSiMe₃)₂ (R²= CH₃, CF₃) reacted with the ketimine, CH₃C(=NiPr)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 (Me₃SiO)₃P furnished either a mono (R^F = CF₃) 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 (see Scheme 2) Acetyl phosphonates, at the double bond. $R^2C(=O)P(=O)(OSiMe_3)$, ($R^2 = CH_3$, CF_3) were easily prepared and could be reacted further with (Me₃SiO)₃P to yield bisphosphonates, which after hydrolysis were transformed into the respective free acids. [5] However, the compounds $R^2C(=O)P(=O)(OSiMe_3)_2$ ($R^2 = CH_3$, CF₃) were considered analogues of CH₃COCF₃ and CF₃COCF₃ taking the electron-withdrawing capability of the (R¹O)₂P(=O) group into account, [2] therefore, ketimines in their enamine tautomeric formed addition products. (see Scheme 3)

$$P(OSiMe_3)_3 \xrightarrow{F} F$$

$$R^F = F, CF_3$$

$$P(OSiMe_3)_3, R^F = F \xrightarrow{F} F$$

$$Me_3SiO \xrightarrow{H} F$$

$$Me_$$

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)

$$R^2$$
 = Me, CF_3

Scheme 3

HO
$$CF_3$$
 OH H CF_3 O= $P(OSiMe_3)_2$

EtO $P(O)(OEt)_2$ Me₃SiO CF_3

Me

Me

Me₃SiO CF_3

Scheme 4

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