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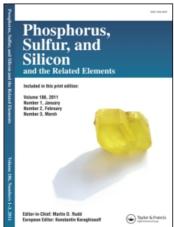
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The Chemistry of Some Isopolar Analogues of Phosphoric and Pyrophosphoric Acids

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The Chemistry of Some Isopolar Analogues of Phosphoric and Pyrophosphoric Acids

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We have previously established that the α -fluorination of alkanephosphonates provides analogues of phosphate esters which have improved 'isopolarity' relative to simple alkanephosphonates. This property is manifest, inter alia, in enhanced acidity and in the upfield shift for the ³¹P n.m.r. resonance. Indeed, for a range of halomethanephosphonic acids we have found the relationship " $\delta_{\rm p} = 9.61({\rm pK_{a^2}} - 4.59){\rm ppm}$ " gives an excellent correlation between these parameters. In this context, the properties of CF₂C1PO(OR)₂ species, derived from the Michaelis-Becker reaction of dialkyl phosphonates with Freon 22, CF₂Cl₂, will be described.

In studies on the development of new methods for the preparation of fluoromethylenebisphosphonates, we have reacted tetraethyl diazomethylenebisphosphonate with hydrogen fluoride under a variety of conditions and will describe novel syntheses of bromofluoromethylene- and chlorofluoromethylenebisphosphonates.

For biological purposes, non-isosteric isopolar analogues of pyrophosphoric acid also have an important role. We have isolated and characterised tetraethyl cis-ethylene-1,2-bisphosphonate as the major reduction product of the corresponding acetylenebisphosphonate. The same cis-isomer is formed by the acid-catalysed cleavage of the 2-ethoxy-1,3-dioxolane derived from Mikroyannidis' tetramethyl 1,2-dihydroxyethane-1,2-bisphosphonate, which is thereby proven to be the meso-isomer. We have isolated the racemic modification of the same ester from the reaction of glyoxal with trimethylphosphite. It is converted via the 1,3-dioxolane into the transisomer of ethylene-1,2-bisphosphonate.

Some of these analogues of pyrophosphoric acid have been incorporated into analogues of nucleoside polyphosphates. $^{1}J.C.S.Perkin\ Trans\ I$, 1984,1119. $^{2}J.C.S.Perkin\ Trans\ I$, submitted.

³Phosphorus & Sulphur, 1984,20,323.