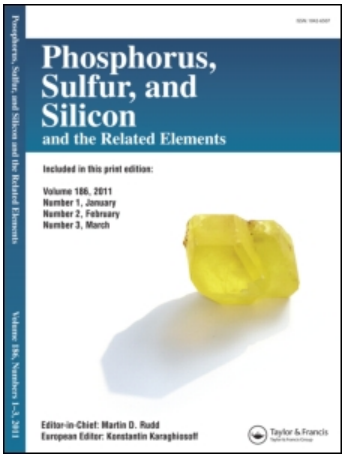

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

The Chemistry of Some Isopolar Analogues of Phosphoric and Pyrophosphoric Acids

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To cite this Article Blackburn, G. Michael , Cumming, Andrew S. and Taylor, Graham E.(1987) 'The Chemistry of Some Isopolar Analogues of Phosphoric and Pyrophosphoric Acids', Phosphorus, Sulfur, and Silicon and the Related Elements, 30: 3, 826
To link to this Article: DOI: 10.1080/03086648708079316
URL: http://dx.doi.org/10.1080/03086648708079316

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.[1] This property is manifest, *inter alia*, in enhanced acidity and in the upfield shift for the ^{31}P n.m.r. resonance. Indeed, for a range of halomethanephosphonic acids we have found the relationship " $\delta_P = 9.61(pK_{a2} - 4.59)$ppm " gives an excellent correlation between these parameters. In this context, the properties of $CF_2ClPO(OR)_2$ species, derived from the Michaelis-Becker reaction of dialkyl phosphonates with Freon 22, CF_2Cl_2, 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,[3] 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 *trans*-isomer 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.*
[3] *Phosphorus & Sulphur*, 1984, **20**, 323.