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Synthesis of Some Mixed Dialkyl Phosphites and their Use as Forerunners for Potential Chiral Phosphates

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Organophosphorus compounds containing a chiral centre at the P atom are of considerable interest from a stereochemical point of view. Accordingly, trialkyl phosphates (RO)(R₁O)(R₂O)P(O) (4) were synthesized starting from dialkyl phosphites. Thus: direct hydrolysis of dialkyl phosphites (RO)₂P(O)H (1) with tetraethylammonium hydroxide (20% aqueous solution), followed by extraction with dichloromethane affords the corresponding tetraethylammonium alkyl hydrogen phosphites (2). Good yields (η) of mixed dialkyl phosphites (3) were obtained on heating stoichiometric amounts of (2) and alkyl iodides in acetonitrile solution at 60° C, for 6 hrs. Mixed dialkyl phosphites (3) were used in synthesis of some trialkyl phosphates (4) by PTC (see scheme).

Table 1. Preparation of tetraethylammonim hidrogen phosphites (2), mixed dialkyl phosphites (3) and mixed trialkyl phosphates (4)

Product no.	R	R_1	R ₂	³¹ P-NMR (δ, ppm)	Yield,%
2.a.	C ₂ H ₅		-	•	70
2.b.	n-C ₄ H ₉		-	•	90
3.a.	C ₂ H ₅	CH ₃	•	-4,3	49
3.b.	C ₂ H ₅	n-C ₄ H ₉	_	-6,6	73
3.c.	n-C ₄ H ₉	C ₂ H ₅	-	-6,6	68
4.a.	C ₂ H ₅	CH ₃	n-C ₃ H ₇	+0,89	68
4.b	C ₂ H ₅	n-C4H9	n-C ₃ H ₇	+1,00	80
4.c.	n-C ₄ H ₉	C ₂ H ₅	n-C ₃ H ₇	+1,00	65

The synthetised compounds were analysed by IR and ³¹P-NMR spectroscopy. These syntheses shown:

- a new facile route for synthesis of mixed dialkyl phosphites;
- synthesis of mixed trialkyl phosphates, with three different radicals, by phase transfer catalysis;
- new possibilities for synthesis of chiral phosphorus compounds.