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Two step acidic hydrolysis of dialkyl arylphosphonates

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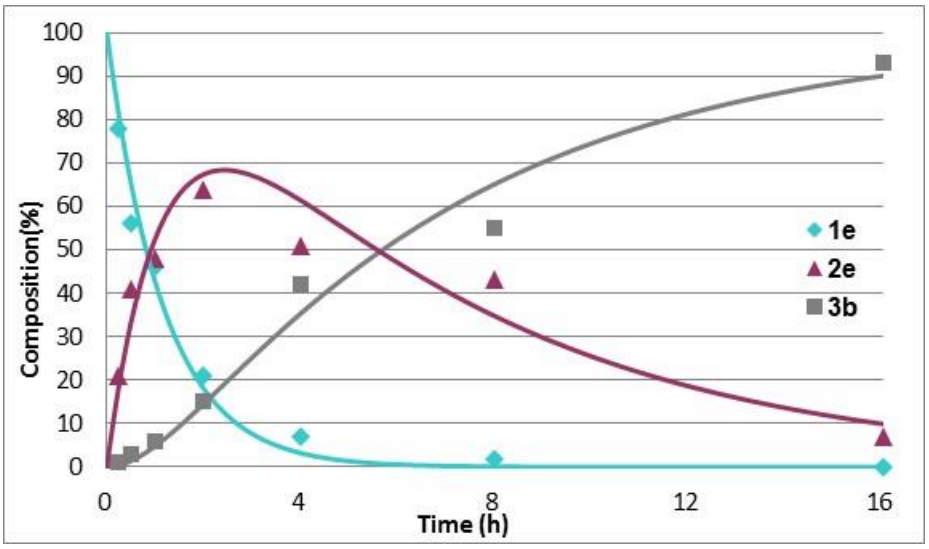

Figure S1 Concentration profile for the components during the hydrolysis of diethyl 4-methylphenylphosphonate **1e** under optimum conditions. The R^2 measure of goodness of fit is 0.965.

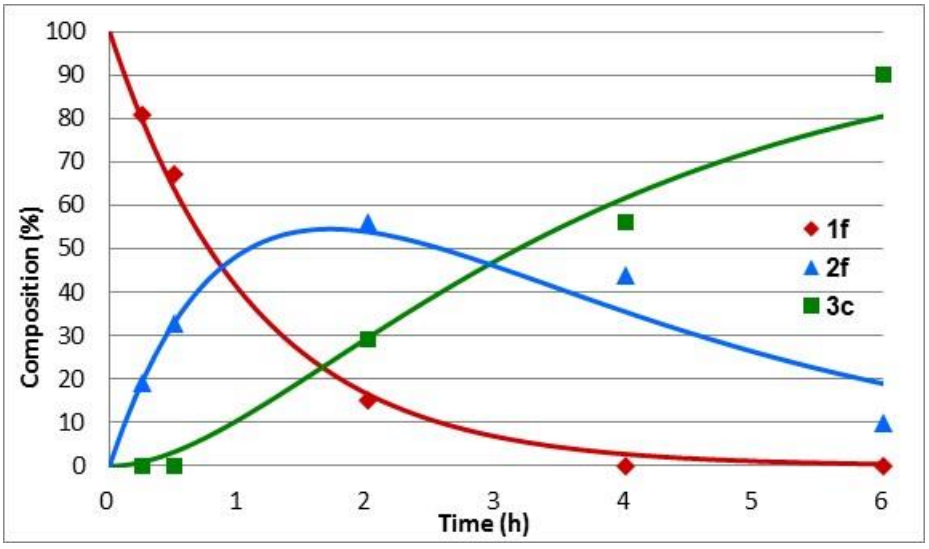

Figure S2 Concentration profile for the components during the hydrolysis of diethyl 4-acetylphenylphosphonate **1f** under optimum conditions. The R^2 measure of goodness of fit is 0.977.

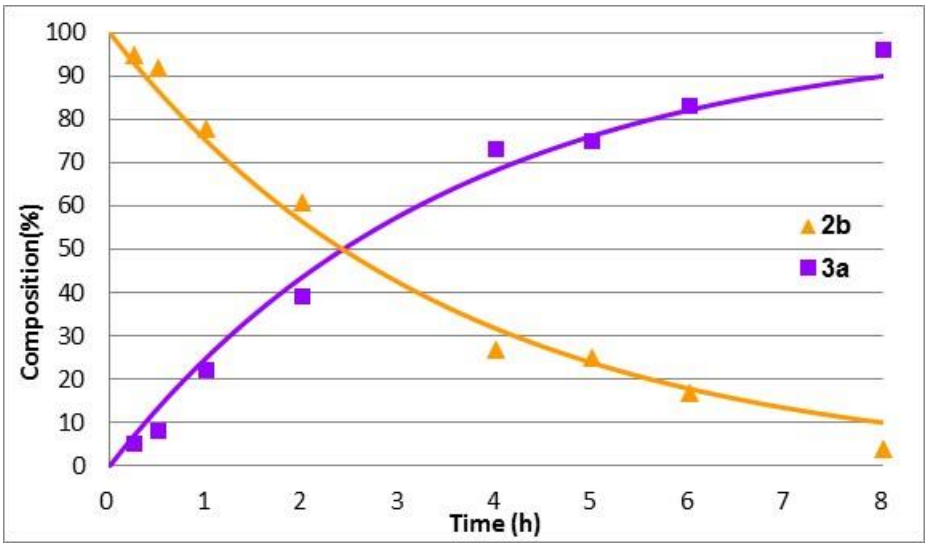

Figure S3 Concentration profile for the hydrolysis of PhP(O)(OEt)(OH) **2b** to $PhP(O)(OH)_2$ **3a**. The R^2 measure of goodness of fit is 0.986.

The ^{31}P NMR spectra were taken on a Bruker DRX-500 spectrometer operating at 202.4 MHz. The couplings are given in Hz. LC-MS experiments were performed with an Agilent 1200 liquid chromatography system coupled with a 6130 quadrupole mass spectrometer equipped with an ESI ion source (Agilent Technologies, Palo Alto, CA, USA). High resolution mass spectrometric measurements were performed using a Q-TOF Premier mass spectrometer in positive electrospray mode.

Evaluation of the ^{31}P NMR spectra. The composition of the reaction mixture was determined by the integration of the corresponding peaks in the ^{31}P NMR spectra, and by peak deconvolution using ACD/Spectrus Processor software package.[S1]

Curve fitting on the time — relative quantity data pairs. The two steps of the acidic hydrolysis were modelled assuming pseudo first order kinetics. The concentration of water and hydrochloric acid was constant during the reaction. The calculated time – composition curves were fitted to the experimental data using non-linear least squares method. The pseudo first order rate constants were optimized that the sum of squares of the residuals (i.e. the difference of the experimental and the calculated composition) to be the minimal. The approximate values of the rate constants were found iteratively, using the Nonlinear Generalized Reduced Gradient method[S2] of Microsoft Excel Solver.

Table S1 Identification of phosphonates **1a-f**, phosphonic ester-acids **2a-f**, and phosphonic acids **3a-c**.

	δ ^{31}P NMR		[M+H][a]
	found	literature	
1a	21.8 ($CDCl_3$)	21.6 ($CDCl_3$)[S3]	187.1
1b	18.8 ($CDCl_3$)	18.9 ($CDCl_3$)[S4]	215.1
1c	15.8 ($CDCl_3$)	16.6 ($CDCl_3$)[S3]	243.1
1d	19.9 ($CDCl_3$)	19.7 ($CDCl_3$)[S3]	339.1
1e	19.6 ($CDCl_3$)	20.6 ($CDCl_3$)[S4]	229.1
1f	17.0 ($CDCl_3$)	16.9 ($CDCl_3$)[S4]	257.1
2a	16.4 (DMSO)	19.6[b,S5]	173.1
2b	15.0 (DMSO)	20.4 ($CDCl_3$)[S6]	187.1
2c	14.1 (DMSO)	15.7[b,S5]	201.1
2d	15.4 (DMSO)	21.7 ($CDCl_3$)[S7]	249.1
2e	15.8 (DMSO)	18.1 ($CDCl_3$)[S7]	201.1
2f	13.2 (DMSO)	19.0 ($CDCl_3$)[S6]	228.1
3a[c,d]	13.0 (DMSO)	14.6 (DMSO)[S8]	159
3b[c,e]	13.6 (DMSO)	14.0 (DMSO)[S4]	173
3c[c,f]	11.1 (DMSO)	16.9 (DMSO)[S4]	201

[a]Obtained by LC-MS.
[b]No solvent was provided.
[c]The solid residue was recrystallized from MeOH.
[d]mp: 157–158 °C, mp[S4]: 150–152 (dec)
[e]mp: 173–175 °C, mp[S4]: 172–174 (dec)
[f]mp: 160–162 °C, mp[S4]: 157–159 (dec)

References

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