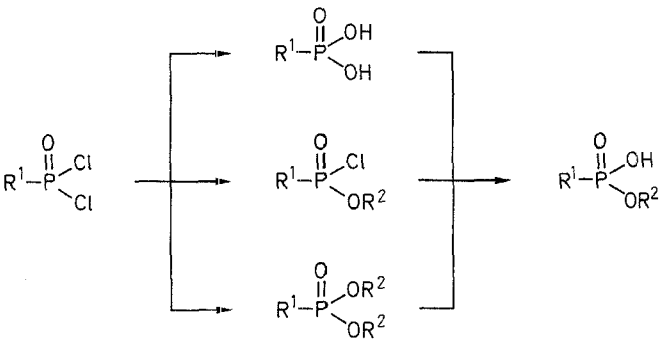
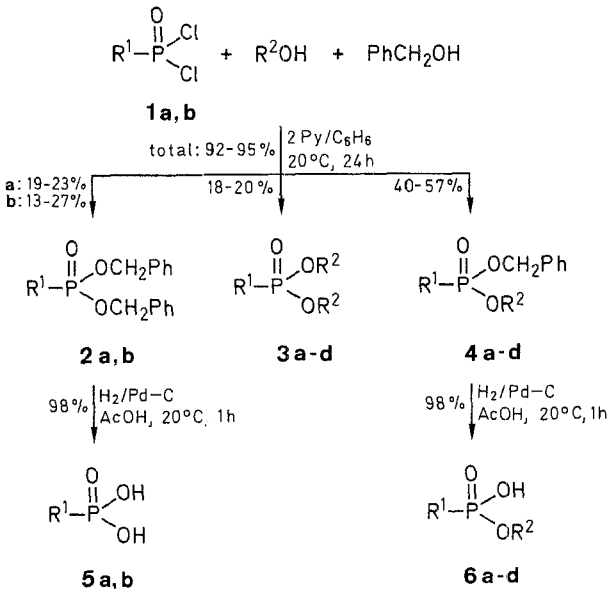


Here we give a simplified methodology to reach the same products starting from the same substrate. The method utilizes the well known ability of the benzyl protective group to be removed by hydrogenolysis from phosphoric[2] or phosphonic[3] benzyl esters.

The first step consists of alcoholysis of the starting dichloride **1** in the presence of an acid acceptor, using one molecular equivalent each of benzyl alcohol and any other alcohol; this procedure affords a mixture of three diesters (the two symmetric esters **2** and **3** and the unsymmetric ester **4**) chromatography of which gives the pure individual esters. Hydrogenolysis of esters **2** and **4** then affords the phosphonic acid **5** and the monoester **6**.



1, 2, 5	R^1	3, 4, 6	R^1	R^2
a	Ph	a	Ph	n-$C_{14}H_{29}$
b	$ClCH_2CH_2$	b	$ClCH_2CH_2$	n-$C_{14}H_{29}$
		c	Ph	$(CH_2CH_2O)_2CH_3$
		d	$ClCH_2CH_2$	$(CH_2CH_2O)_2CH_3$

The process was first performed with phenylphosphonic dichloride (**1a**), using either tetradecanol or 2-(2-methoxyethoxy)ethanol as R^2OH. It was then applied to 2-chloroethylphosphonic dichloride, thus leading to compounds which are analogous to the agrochemical "ethephon". The phosphonic diacids **5a** and **5b** have already been described.[4,5]

An Improved Access to Phosphonic Acids and Their Mono- and Diesters

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The reaction of phosphonic dichlorides with a mixture of benzyl alcohol and an aliphatic alcohol affords a mixture of the corresponding dibenzyl phosphonate, dialkyl phosphonate, and alkyl benzyl phosphonate which is easily separated by column chromatography to give the pure components. Cleavage of the dibenzyl phosphonate by catalytic hydrogenation affords the phosphonic acid whereas cleavage of the alkyl benzyl phosphonate under the same conditions affords the alkyl hydrogen phosphonate (monoester).

Starting from a parent phosphonic dichloride, the access to each of the three corresponding acid, the monoester, and the diester usually requires separate procedures.[1]

Table 1. Phosphonic Acid Diesters **2**, **3**, and **4** Prepared from Phosphonic Dichlorides **1**, Benzyl Alcohol, and a Second Alcohol

Dichloride	Mixture of Alcohols	Products	Yield[a] (%)	Molecular Formula[b]	MS[c] *m/z*
1a	$PhCH_2OH$ + n-$C_{14}H_{29}OH$	**2a**	19	$C_{20}H_{19}O_3P$ (338.3)	339
		3a	20	$C_{34}H_{63}O_3P$ (550.8)	551
		4a	42	$C_{27}H_{41}O_3P$ (444.6)	444
1a	$PhCH_2OH$ + $CH_3(OCH_2CH_2)_2OH$	**2a**	23	see above	
		3c	18	$C_{16}H_{27}O_7P$ (362.35)	363
		4c	57	$C_{18}H_{23}O_5P$ (350.3)	351
1b	$PhCH_2OH$ + n-$C_{14}H_{29}OH$	**2b**	27	$C_{16}H_{18}ClO_3P$ (324.7)	325
		3b	19	$C_{30}H_{62}ClO_3P$ (537.2)	537
		4b	40	$C_{23}H_{40}ClO_3P$ (431.0)	431
1b	$PhCH_2OH$ + $CH_3(OCH_2CH_2)_2OH$	**2b**	13	see above	
		3d	20	$C_{12}H_{26}ClO_7P$ (348.75)	349
		4d	48	$C_{14}H_{22}ClO_5P$ (336.75)	337

[a] Yield of isolated pure product. All products **2**, **3**, and **4** were obtained as oils.
[b] Satisfactory microanalyses obtained: C ±0.39, H ±0.35. Exception: **3d**, C −0.48.
[c] FAB technique on a JEOL DX 300 spectrometer.

Table 2. Phosphonic Acid Monoesters **6** Prepared

Product	Yield[a] (%)	mp (°C)	Molecular Formula[b]	MS[c] *m/z*
6a	98	oil	$C_{20}H_{35}O_3P$ (354.45)	355
6b	98	33	$C_{16}H_{34}ClO_3P$ (340.9)	341
6c	98	oil	$C_{11}H_{17}O_5P$ (260.2)	260
6d	98	oil	$C_7H_{16}ClO_5P$ (246.6)	247

[a] Yield of isolated pure product.
[b] Satisfactory microanalyses obtained (except for 2 values): C +0.50, H ±0.33; unsatisfactory: **6c**, C +0.50; **6d**, C-0.52.
[c] FAB technique on a JEOL DX 300 spectrometer.

Dibenzyl 2-Chloroethylphosphonate (2b), Ditetradecyl 2-Chloroethylphosphonate (3b), and Benzyl Tetradecyl 2-Chloroethylphosphonate (4b); Typical Procedure:

Under N_2 at 20°C, 2-chloroethylphosphonic dichloride[4] (**1b**; 5.4 g, 29 mmol) is added to a stirred mixture of anhydrous benzyl alcohol (8.1 g, 29 mmol), tetradecanol (6.2 g, 29 mmol), and pyridine (4.6 g, 58 mmol) in anhydrous benzene (20 mL), and stirring is continued at 20°C for 24 h. Pyridine hydrochloride is filtered off and the filtrate is evaporated. The pure components of the residue are isolated by preparative HPLC (silica gel, hexane/acetone, 7:3).

Tetradecyl 2-Chloroethylphosphonate (6b); Typical Procedure:

A mixture of diester **4b** (1.02 g, 2.39 mmol) and 10% Pd on activated coal (78 mg) in AcOH (100 mL) is hydrogenated at 20°C and atmospheric pressure. After 1 h, the theoretical amount of H_2 (53.5 mL) has been absorbed. The coal is filtered off. Evaporation of the filtrate gives **6b**; yield: 0.81 g (~100%); mp 33°C.

Table 3. Spectral Data of Phosphonic Acid Diesters **2**, **3**, and **4** and Monoesters **6**

Compound	IR (CCl_4)[a] $\nu_{P=O}$ (cm^{-1})	^{1}H-NMR ($CDCl_3$)[b] δ, J (Hz)	^{31}P-NMR ($CDCl_3$/85% $H_3PO_{4\,ext}$)[c] δ
2a	1255	5.1 (d, 4H, J = 8); 7.2–8.2 (m, 15H)	19.5
3a	1250	0.7–2.5 (m, 54H); 4.1 (q, 4H, J = 6.5); 7.3–8.1 (m, 5H)	18.7
4a	1253	0.7–2.2 (m, 27H); 4.1 (q, 2H, J = 6.5); 5.1 (de, 2H, J = 8); 7.3–8.1 (m, 10H)	19.0
3c	1250	3.4 (s, 6H); 3.6 (m, 12H); 4.2 (m, 4H); 7.3–8.2 (m, 5H)	18.8
4c	1255	3.4 (s, 3H); 3.6 (m, 6H); 4.2 (m, 2H); 5.1 (d, 2H, J = 8); 7.2–8.2 (m, 10H)	19.2
2b	1245	2.2 (m, 2H); 3.6 (dt, 2H, J = 9, 7); 5.0 (d, 2H, J = 8); 7.4 (s, 10H)	26.6
3b	1243	0.7–2.5 (m, 56H); 3.5–4.3 (m, 6H)	25.4
4b	1246	0.7–1.8 (m, 27H); 2.3 (m, 2H); 3.4–4.2 (m, 4H); 5.1 (d, 2H, J = 9); 7.3 (s, 5H)	26.0
3d	1243	2.4 (m, 2H); 3.4 (s, 6H); 3.3–4.5 (m, 18H)	26.5
4d	1245	2.3 (m, 2H); 3.4 (s, 3H); 3.6 (m, 6H); 4.1 (m, 2H) 5.1 (s, 5H)	26.9

[a] Recorded on a Perkin-Elmer 377 Infrared spectrophotometer.
[b] Recorded on a Varian EM 360 spectrometer.
[c] Recorded on a Bruker WP 80 spectrometer.

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