

Scheme 2.

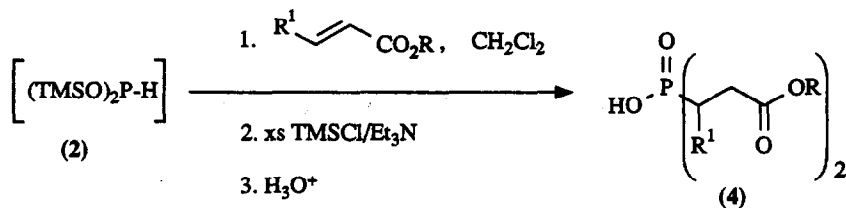




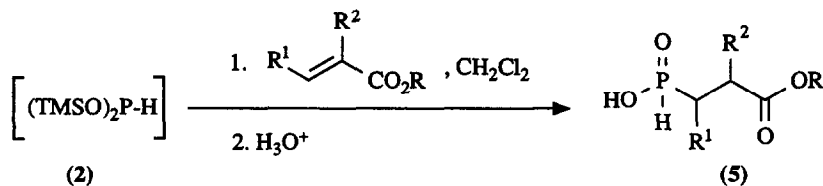


Table 1

Acrylate	R	R ¹	Yield ⁹ (%)
MeO ₂ C 	Me	H	90
EtO ₂ C 	Et	H	82
t-BuO ₂ C 	t-Bu	H	78
EtO ₂ C 	Et	Et	77

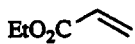
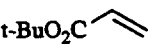
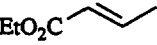
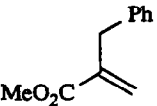
amount of acrylate with which to react, hence no contamination with disubstituted phosphinic acid resulting from a second addition to acrylate was observed. Simple acidic work-up resulted in mono-substituted phosphinic acids (5) as viscous, colourless oils. The reaction is shown in Scheme 3, and examples in Table 2.

Scheme 3.



Synthesis of unsymmetrical disubstituted phosphinic acids was achieved by taking a previously synthesized mono-substituted phosphinic acid (5), and subjecting it to the silylating conditions (TMSCl/NEt₃)⁸ to form the probable intermediate (6), followed by addition of the chosen acrylate and acidic work-up, to give the appropriate disubstituted phosphinic acid (7) (Scheme 4). Examples are shown in Table 3.

Table 2

Acrylate	R	R ¹	R ²	Yield ⁹ (%)
	Et	H	H	85
	t-Bu	H	H	78
	Et	Me	H	74
	Me	H	Bn	81

Scheme 4.

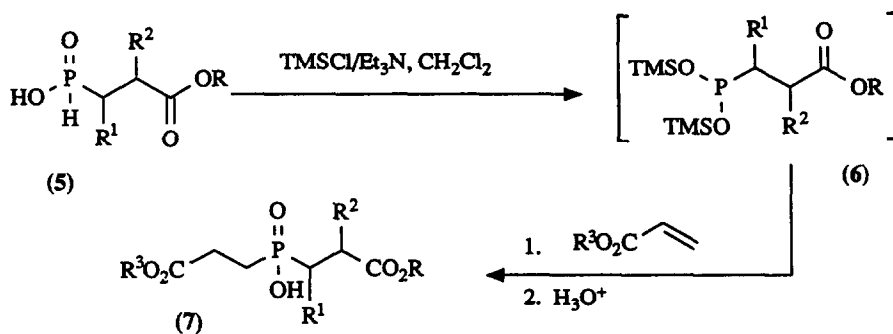
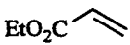
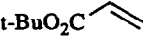
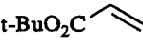


Table 3

Mono-substituted Phosphinic acid (5)			acrylate	Disubstituted Phosphinic acid (7)	yield ⁹ (%)
R	R ¹	R ²		R ³	
t-Bu	H	H		Et	75
Me	H	Bn		t-Bu	63
Et	Me	H		t-Bu	77

Typical Experimental Procedure.^{9,10}**1. Symmetrical disubstituted phosphinic acids (4).**

To a stirred solution of (1) (1.0 g, 5.99 mmol) in dry CH_2Cl_2 (30 ml) at 0 °C, was added a 1:1 mixture of chlorotrimethylsilane and triethylamine ($\text{TMSCl}/\text{Et}_3\text{N}$)⁸ (6.0 ml, 18 mmol, 3.5 eq. of each), at less than 5 °C. After 1-2 h the acrylate (2.2 eq.) was added at 0 °C, stirred for 0.5 h, allowed to warm to room temperature and stirred overnight. The reaction was filtered, dilute hydrochloric acid added, and extracted with CH_2Cl_2 to give the crystalline disubstituted phosphinic acid (4) which was purified by trituration with hexane/ether.

2. Mono-substituted phosphinic acids (5).

To a stirred solution of (1) (5.0 g, 29.9 mmol, 5 eq.) in dry CH_2Cl_2 (100 ml) at 0 °C, was added a 1:1 mixture of chlorotrimethylsilane and triethylamine (20 ml, 12 eq.). The acrylate (1.0 eq.) was added at 0 °C, stirred for 0.5 h, then allowed to warm to room temperature overnight. The reaction was filtered and dilute hydrochloric acid work-up followed by dichloromethane extraction yielded the phosphinic acid (5) as an oil.

3. Unsymmetrical disubstituted phosphinic acids (7).

To a solution of the appropriate mono-substituted phosphinic acid (5) (4.0 mmol, 1 eq.) in dry CH_2Cl_2 (30 ml) was added a 1:1 mixture of chlorotrimethylsilane and triethylamine (7 ml, 4 eq.) at 0 °C. After stirring for 1 h the appropriate acrylate (4.4 mmol, 1.1 eq.) was added, the reaction allowed to warm to room temperature, and stirred overnight. Filtration followed by acidic work-up and dichloromethane extraction yielded the disubstituted phosphinic acid (7) which was purified by trituration with hexane/ether.

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- $\text{TMSCl}/\text{Et}_3\text{N}$, equivalent molar amounts, were mixed under nitrogen and centrifuged to allow removal of the supernatant, leaving behind a (copious) triethylammonium chloride precipitate.
- Satisfactory IR, NMR (^1H , ^{13}C , and ^{31}P), MS and/or elemental analysis were obtained for all new compounds.
- All the apparatus was meticulously dry and clean. All reactions were carried out under a dry nitrogen atmosphere.