One-pot synthesis of vinyl phosphonates from 2-hydroxyalkyl phenyl selenides with monoethyl esters of phosphonic acid

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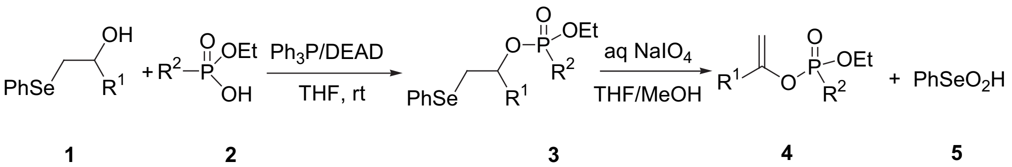
Vinyl phosphonates were prepared with good yields in a one-pot, two-step transformation by Mitsunobu reaction of 2-hydroxyalkyl phenyl selenides with monoethyl esters of phosphonic acid followed by oxidation-elimination.

Keywords: 2-hydroxyalkyl phenyl selenide, monoethyl esters of phosphonic acid, Mitsunobu condition, vinyl phosphonate, oxidation-elimination

Organophosphonates are an important class of intermediates in the synthesis of biologically active compounds and are generally prepared by the Arbuzov reaction.[1] Vinyl phosphonates are important pesticides with widely applicable insecticides properties.[2] Recently, some new vinyl phosphonates have been reported as potent mechanism-based inhibitors of phosphatase[3] or phosphodiesterase.[4] However, there are only a few reports about the synthesis and bioactivity of their analogues with C-P bond, vinyl phosphonates, which have been found to have insecticidal[5] and antifungal[6] activity. Vinyl phosphonates are usually prepared by Perkow-type reaction[7] between phosphonites and α-halocarbonyl compounds, but this procedure often gives a mixture.[8] One strategy for the synthesis of vinyl phosphonates comprises the addition of phosphonic acid to alkynes. Wasserman[9] previously prepared a few alkoxyvinyl phosphates by the reactions of phosphoric acid diesters with ethoxyacetylene in the presence of Hg $(OAc)_2$. In 1998, Hua *et al.*[10] developed the ruthenium-catalysed addition reaction of diphenylphosphinic acid to terminal alkynes. Recently, Hg $(OAc)_2/BF_3{\cdot}OEt$ promoted reaction of monoesters of phosphonic acid with terminal alkynes was reported for regioselective synthesis of vinyl phosphonates.[11] However, these methods involved difficulties such as harsh reactions, laborious manipulation and low overall yields, or in some cases, highly toxic compounds are used or some reagents such as terminal alkynes and ruthenium-catalyst are not readily available. Therefore, exploring more efficient, experimentally simple methodology is still interesting. Organoselenium reagents are now commonly used as powerful tools for introducing new functional groups into organic substrates under extremely mild conditions.[12,13] For example, the phenylseleno group is readily converted to a leaving group giving access to carbon–carbon double bond *via* oxidation followed by β-elimination.[14] β-Hydroxyalkyl selenides are valuable selenium intermediates in organic synthesis, they can be converted to allylic alcohols, olefins, bomohydrins and vinyl selenides, epoxide,[15] and can be used to prepare tetrahydrofuran derivatives[16] and some other important nature products,[17] *etc.* On the other hand, the Mitsunobu reaction has found extensive use in organic synthesis over the past two decades, particularly for the inversion of the stereochemistry of alcohols *via* an esterification procedure.[18] Based on these and in continuation of our interest in organoselenium chemistry,[19] we designed a novel, convenient, and efficient one-pot, two-step route for the preparation of vinyl phosphonates by the Mitsunobu reaction of 2-hydroxyalkyl phenyl selenides with monoethyl esters of phosphonic acid followed by oxidation-elimination (Scheme 1).

2-Hydroxyalkyl phenyl selenides (**1a**, **1b** and **1c**) could be easily obtained by the reaction of benzeneselenolate ions with the corresponding epoxides[20] in ethanol at ambient temperature in 54%, 90% and 88%, respectively. With compounds **1a**–**1c** in hand, the preparation of intermediate selenides **3**, the key for the success of this protocol was investigated from 2-hydroxy-2-phenylethyl phenyl selenide (**1a**) with monoethyl esters of phenylphosphonate (**2a**). Firstly, esterification reaction of **1a** and **2a** was carried out with condensing reagents (DCC), but the yield of corresponding product **3a** was about 60%, and a large excess of both DCC and substrate **1a** are required. In addition, forcing conditions are required heating to reflux temperature in a solution of THF and triethylamine. This prompted the search for a mild coupling reaction that would consistently produce high yields. It is well known that the Mitsunobu reaction is a mild and effective method utilising the redox chemistry of triphenylphosphine and a dialkyl azodicarboxylate to condense an acidic reagent with primary and secondary alcohols. After a series of experiments, we found that the Mitsunobu reaction provides a convenient and efficient route to **3a** in 88% yield. Although selenated intermediates **3a** can be isolated and purified by chromatography, we have found it most convenient to carry out the oxidation of these materials in one-pot. Mild oxidation of the selenide **3a** and elimination of the selenoxide provided vinyl phosphonate (**4a**) in 84% yield. After successfully the initial studies of preparation of 4a, extension of this method to the synthesis of other analogues in moderate to good yields was investigated (Table 1). The phenylseleno moiety, introduced in the starting material is eliminated as benzeneseleninic acid (**5**) in the oxidation step. After addition of K_2CO_3 the water-soluble potassium benzeneseleninate could be separated. From this diphenyl diselenide was recovered in good yield.

In summary, we have developed a novel and convenient method for the preparation of vinyl phosphonates with good yields in a one-pot, two-step transformation employing



Scheme 1

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Mitsunobu reaction of 2-hydroxyalkyl phenyl selenides with monoethyl esters of phosphonic acid followed by oxidation-elimination.

Experimental

Melting points were uncorrected. ^{1}H NMR (400 MHz) spectra were recorded on a Bruker Avance (400 MHz) spectrometer, using $CDCl_3$ as the solvent and TMS as internal standard. FT-IR spectra were taken on a Perkin-Elmer SP One FT-IR spectrophotometer. Microanalyses were performed with a PE 2400 elemental analyser. MS spectra were determined using a HP5989A mass Spectrometer. Solvents were purified and dried according to standard procedures. Mono ethyl esters of phosphonic acid **2** were prepared according to the procedure described in literatures.[21-24] Other reagents were commercially obtained.

General procedure for the preparation of vinyl phosphonates (**4a–4m**)

To a solution of 2-hydroxyalkyl phenyl selenide **1** (1.0 mmol) and monoester of phosphonic acid **2** (1.0 mmol) in dry THF (20 ml) at room temperature under nitrogen was added PPh_3 (525 mg, 2.0 mmol), followed by the dropwise addition of diethyl azodicarboxylate (DEAD) (316 μL, 2.0 mmol). The reaction mixture was stirred until TLC analysis showed that the starting selenide was completely conversion into the corresponding selenated intermediates **3** (3–4 h). Then aqueous $NaIO_4$ (4.0 mmol) and MeOH (10 ml) was added to the reaction mixture, and stirred at room temperature until the reaction was finished as determined by TLC (2–2.5 h). Powered K_2CO_3 (0.53 g, 5 mol) was then added to the reaction mixture and stirred at room temperature and the mixture was extracted with ether (20 × 3 ml). The combined organic phase was washed with saturated $NaHCO_3$ solution, brine and twice water and then dried over magnesium sulfate. The solvent was removed in vacuo and the residue was purified by column chromatography on silica gel using hexane/ethyl acetate (5:1–2:1) as eluent to give **4a–4m** as colourless oils except for **4d** and **4h**.

Ethyl 1-phenylethenyl phenylphosphonate (**4a**): Colourless oil (Lit.[11] oil); ^{1}H NMR: δ = 7.92–7.85 (m, 2H), 7.60–7.34 (m, 8H), 5.22 (t, $J_{HH} = J_{PH}$ = 2.3 Hz, 1H), 5.18 (t, $J_{HH} = J_{PH}$ = 2.3 Hz, 1H), 4.30–4.24 (m, 2H), 1.35 (t, J = 7.2 Hz, 3H); IR (film): ν = 2984, 1632, 1392, 1256, 1130, 1041, 990, 822 cm^{-1}.

Ethyl 1-phenylethenyl p-methylphenylphosphonate (**4b**): Colourless oil (Lit.[11] oil); ^{1}H NMR: δ = 7.80–7.74 (m, 2H), 7.60–7.53 (m, 2H), 7.37–7.25 (m, 5H), 5.22 (t, $J_{HH} = J_{PH}$ = 2.4 Hz, 1H), 5.19 (t, $J_{HH} = J_{PH}$ = 2.4 Hz, 1H), 4.29–4.20 (m, 2H), 2.41 (s, 3H), 1.36 (t, J = 7.2 Hz, 3H); IR (film): ν = 2984, 1633, 1392, 1254, 1130, 1041, 990, 824 cm^{-1}.

Ethyl 1-phenylethenyl p-chlorophenylphosphonate (**4c**): Colourless oil (Lit.[11] oil); ^{1}H NMR: δ = 7.85–7.78 (m, 2H), 7.55–7.51 (m, 2H), 7.47–7.42 (m, 2H), 7.37–7.35 (m, 3H), 5.25 (t, $J_{HH} = J_{PH}$ = 2.4 Hz, 1H), 5.18 (t, $J_{HH} = J_{PH}$ = 2.4 Hz, 1H), 4.30–4.22 (m, 2H), 1.36 (t, J = 7.2 Hz, 3H); IR (film): ν = 2984, 1633, 1391, 1256, 1090, 1040, 992, 821 cm^{-1}.

Ethyl 1-phenylethenyl p-nitrophenylphosphonate (**4d**): Yellow solid, m.p. 97–98°C (Lit.[11] mp. 97°C); ^{1}H NMR: δ = 8.34–8.30 (m, 2H), 8.11–8.06 (m, 2H), 7.55–7.50 (m, 2H), 7.34–7.34 (m, 3H), 5.27 (t, $J_{HH} = J_{PH}$ = 2.6 Hz, 1H), 5.20 (t, $J_{HH} = J_{PH}$ = 2.6 Hz, 1H), 4.38–4.31 (m, 2H), 1.38 (t, J = 7.2 Hz, 3H); IR (KBr): ν = 2986, 1640, 1525, 1268, 1128, 1030, 976, 886 cm^{-1}

Ethyl 1-phenylethenyl benzylphosphonate (**4e**): Colourless oil (Lit.[11] oil); ^{1}H NMR: δ = 7.46–7.41 (m, 2H), 7.32–7.26 (m, 8H), 5.27 (t, $J_{HH} = J_{PH}$ = 2.5 Hz, 1H), 5.20 (t, $J_{HH} = J_{PH}$ = 2.5 Hz, 1H), 4.16–4.02 (m, 2H), 3.34 (d, J_{PH} = 10.5 Hz, 2H), 1.23 (t, J = 7.1 Hz, 3H); IR (film): ν = 2983, 1632, 1391, 1260, 1100, 1040, 992, 851 cm^{-1}.

Ethyl phenyllethenyl n-butylphosphonate (**4f**): Colourless oil (Lit.[11] oil); ^{1}H NMR: δ = 7.61–7.57 (m, 2H), 7.42–7.36 (m, 3H), 5.29 (t, $J_{HH} = J_{PH}$ = 2.4 Hz, 1H), 5.25 (t, $J_{HH} = J_{PH}$ = 2.4 Hz, 1H), 4.30–4.07 (m, 2H), 2.00–1.87 (m, 2H), 1.76–1.60 (m, 2H), 1.47–1.39 (m, 2H), 1.33 (t, J = 7.1 Hz, 3H), 0.93 (t, J = 7.2 Hz, 3H); IR (film): ν = 2950, 1633, 1393, 1250, 1097, 1040, 992, 821 cm^{-1}.

Ethyl 1-phenoxymethylethenyl p-methylphenylphosphonate (**4g**): Colourless oil; ^{1}H NMR: δ = 7.81–7.75 (m, 2H), 7.59–7.53 (m, 2H), 7.49–7.38 (m, 2H), 7.19–7.10 (m, 3H), 5.24 (t, $J_{HH} = J_{PH}$ = 2.4 Hz, 1H), 5.19 (t, $J_{HH} = J_{PH}$ = 2.4 Hz, 1H), 4.28–4.21 (m, 2H), 3.26–3.23 (m, 2H), 2.41 (s, 3H), 1.35 (t, J = 7.1 Hz, 3H); ^{13}C NMR: δ = 155.5 (d, J_{CP} = 9.3 Hz), 134.4 (d, J_{CP} = 3.0 Hz), 131.7 (d, J_{CP} = 10.1 Hz), 129.4, 128.8 (d, J_{CP} = 15.4 Hz), 126.9, 125.1 (d, J_{CP} = 192.4 H), 121.0, 114.6, 97.0 (d, J_{CP} = 4.6 H), 65.9 (d, J_{CP} = 4.8 H), 62.2 (d, J_{CP} = 6.4 H), 21.1, 16.2 (d, J_{CP} = 6.3 H); IR (film): ν = 2985, 1635, 1393, 1255, 1243, 1130, 1094, 1045, 991, 825 cm^{-1}; MS: *m/z* (%) = 332 [M$^+$]; Anal. Calcd for $C_{18}H_{21}PO_4$: C, 65.05; H, 6.37. Found: C, 65.12; H, 6.42.

Table 1 One-pot synthesis of vinyl phosphonates **4a–4m**

Entry	R^1 (**1**)	R^2 (**2**)	Product	Yield/ %^{a}
1	C_6H_5 (**1a**)	C_6H_5 (**2a**)	**4a**	84
2	C_6H_5 (**1a**)	p-$CH_3C_6H_4$ (**2b**)	**4b**	82
3	C_6H_5 (**1a**)	p-ClC_6H_4 (**2c**)	**4c**	83
4	C_6H_5 (**1a**)	p-$NO_2C_6H_4$ (**2d**)	**4d**	79
5	C_6H_5 (**1a**)	$C_6H_5CH_2$ (**2e**)	**4e**	78
6	C_6H_5 (**1a**)	n-C_4H_9 (**2f**)	**4f**	81
7	$C_6H_5OCH_2$ (**1b**)	p-$CH_3C_6H_4$ (**2b**)	**4g**	84
8	$C_6H_5OCH_2$ (**1b**)	p-$NO_2C_6H_4$ (**2d**)	**4h**	83
9	n-C_4H_9 (**1c**)	C_6H_5 (**2a**)	**4i**	80
10	n-C_4H_9 (**1c**)	p-$CH_3C_6H_4$ (**2b**)	**4j**	82
11	n-C_4H_9 (**1c**)	p-$NO_2C_6H_4$ (**2d**)	**4k**	79
12	n-C_4H_9 (**1c**)	$C_6H_5CH_2$ (**2e**)	**4l**	78
13	n-C_4H_9 (**1c**)	n-C_4H_9 (**2f**)	**4m**	80

^{a}Isolated yield based on 2-hydroxyalkyl phenyl selenides **1**.

Ethyl 1-phenoxymethylethenyl p-nitrophenylphosphonate (**4h**): Yellow solid (m.p. 103–104°C); ^{1}H NMR: δ = 8.33–8.29 (m, 2H), 8.10–8.05 (m, 2H), 7.50–7.41 (m, 2H), 7.21–7.13 (m, 3H), 5.27 (t, $J_{HH} = J_{PH}$ = 2.7 Hz, 1H), 5.21 (t, $J_{HH} = J_{PH}$ = 2.7 Hz, 1H), 4.38–4.31 (m, 2H), 3.33–3.26 (m, 2H), 1.38 (t, J = 7.5 Hz, 3H); ^{13}C NMR: δ = 156.5 (d, J_{CP} = 9.3 Hz), 135.1 (d, J_{CP} = 3.3 Hz), 132.3 (d, J_{CP} = 10.1 Hz), 130.4, 128.8 (d, J_{CP} = 15.4 Hz), 127.3, 125.2 (d, J_{CP} = 192.4 H), 122.4, 115.8, 97.8 (d, J_{CP} = 4.5 H), 66.1 (d, J_{CP} = 4.9 H), 63.1 (d, J_{CP} = 7.2 H), 16.5 (d, J_{CP} = 6.4 H); IR (film): ν = 2988, 1641, 1525, 1268, 1128, 1033, 975, 885 cm^{-1}; MS: *m/z* (%) = 363 [M$^+$]; Anal. Calcd for $C_{17}H_{18}PNO_6$: C, 56.20; H, 4.99; N, 3.86. Found: C, 56.31; H, 5.08, N, 3.79.

Ethyl n-butylethenyl phenylphosphonate (**4i**): Colourless oil (Lit.[11] oil); ^{1}H NMR: δ = 7.85–7.79 (m, 2H), 7.57–7.46 (m, 3H), 4.76 (t, $J_{HH} = J_{PH}$ = 2.2 Hz, 1H), 4.45–4.43 (m, 1H), 4.24–4.13 (m, 2H), 2.16 (t, J = 7.2 Hz, 2H), 1.51–1.24 (m, 7H), 0.87 (t, J = 7.2 Hz, 3H); IR (film): ν = 2960, 1654, 1390, 1260, 1131, 1042, 995, 860 cm^{-1}.

Ethyl n-butylethenyl p-methylphenylphosphonate (**4j**): Colourless oil (Lit.[11] oil); ^{1}H NMR: δ = 7.79–7.73 (m, 2H), 7.32–7.28 (m, 2H), 4.76–4.72 (m, 1H), 4.45–4.43 (m, 1H), 2.43 (s, 3H), 2.15 (t, J = 7.2 Hz, 2H), 1.47–1.24 (m, 7H), 0.85 (t, J = 7.2 Hz, 3H); IR (film): ν = 2960, 1654, 1455, 1387, 1260, 1130, 1041, 995, 818 cm^{-1}.

Ethyl n-butylethenyl p-nitrophenylphosphonate (**4k**): Colourless oil (Lit.[11] oil); ^{1}H NMR: δ = 8.33–8.29 (m, 2H), 8.09–8.01 (m, 2H), 4.75 (t, $J_{HH} = J_{PH}$ = 2.2 Hz, 1H), 4.50–4.47 (m, 1H), 4.30–4.21 (m, 2H), 2.15 (t, J = 7.2 Hz, 2H), 1.49–1.25 (m, 7H), 0.88 (t, J = 7.2 Hz, 3H); IR (film): ν = 2961, 1655, 1352, 1267, 1128, 1040, 996, 851 cm^{-1}.

Ethyl n-butylethenyl benzylphosphonate (**4l**): Colourless oil; ^{1}H NMR: δ = 7.33–7.30 (m, 2H), 7.28–7.21 (m, 3H), 4.73 (t, $J_{HH} = J_{PH}$ = 2.1 Hz, 1H), 4.48–4.46 (m, 1H), 4.27–4.20 (m, 2H), 3.34 (d, J_{PH} = 10.4 Hz, 2H), 2.14 (t, J = 7.2 Hz, 2H), 1.46–1.22 (m, 7H), 0.85 (t, J = 7.2 Hz, 3H).

^{13}C NMR: δ = 155.5 (d, J_{CP} = 9.4 Hz), 132.8 (d, J_{CP} = 2.9 Hz), 130.7 (d, J_{CP} = 9.5 Hz), 130.0 (d, J_{CP} = 6.9 Hz), 128.5 (d, J_{CP} = 3.4 Hz), 127.1 (d, J_{CP} = 3.9 H), 33.5 (d, J_{CP} = 139.0 H), 63.1 (d, J_{CP} = 7.1 H), 34.6 (d, J_{CP} = 4.2 H), 29.7, 21.9, 16.3 (d, J_{CP} = 6.4 H), 13.8; IR (film): ν = 2958, 1645, 1390, 1262, 1108, 1040, 993, 848 cm^{-1}; MS: *m/z* (%) = 282 [M$^+$]; Anal. Calcd for $C_{15}H_{23}PO_3$: C, 63.82; H, 8.21. Found: C, 63.91; H, 8.30.

Ethyl n-butylethenyl n-butylphosphonate (**4m**): Colourless oil; ^{1}H NMR: δ = 4.71 (t, $J_{HH} = J_{PH}$ = 2.1 Hz, 1H), 4.48–4.45 (m, 1H), 4.28–4.21 (m, 2H), 2.16 (t, J = 7.2 Hz, 2H), 1.98–1.88 (m, 2H), 1.71–1.60 (m, 2H), 1.49–1.25 (m, 9H), 0.92 (t, J = 7.2 Hz, 3H), 0.84 (t, J = 7.2 Hz, 3H); ^{13}C NMR: δ = 151.6 (d, J_{CP} = 9.3 Hz), 132.4 (d, J_{CP} = 3.0 Hz), 62.2 (d, J_{CP} = 6.2 H), 34.6 (d, J_{CP} = 4.2 H), 29.9 (d, J_{CP} = 45.4 H), 29.2, 25.1 (d, J_{CP} = 140.2 H), 23.2 (d, J_{CP} = 17.5 H), 21.6, 16.3 (d, J_{CP} = 6.4 H), 13.8, 13.3 (d, J_{CP} = 5.4 H); IR (film): ν = 2956, 1635, 1380, 1265, 1130, 1041, 995, 845 cm^{-1}; MS: *m/z* (%) = 248 [M$^+$]; Anal. Calcd for $C_{12}H_{25}PO_3$: C, 58.03; H, 10.15. Found: C, 58.13; H, 10.24.

Recovery of diphenyl diselenide: The alkaline aqueous extract from the oxidation procedure (containing the benzeneseleninate anion) was neutralised with conc. HCl and then acidified by further addition of the acid. The resulting suspension was evaporated and the residue was suspended in MeOH (20 ml). Hydrazine monohydrate (3.5 mmol, 0.16 ml) was added gradually to the suspension. Stirring was continued until diphenyl diselenide was formed, as indicated by the yellow colour. The mixture was then concentrated *in vacuo*, poured into water (30 ml) and extracted with Et_2O (3 × 20 ml). The organic layer was dried over anhydrous sodium sulfate and evaporated. Diphenyl diselenide was recovered as a pure compound in 60% yield.

We gratefully acknowledge financial support from the National Natural Science Foundation of China (No.20562005) and NSF of Jiangxi Province (No. 0620021).

Received 30 November 2006; accepted 8 February 2007
Paper 06/4333 doi:10.3184/030823407X198221

References

1 (a) G.M. Kosolapoff and L. Maier, (ed), *Organic phosphorus compounds*; Wiley-Interscience: New York, 1972; (b) D.E.C. Corbridge, *Phosphorus: an outline of its chemistry, biochemistry and uses*, 5thed.; Elsevier: Amsterdam; 1995.

2 R. Engel, In *Handbook of Organophosphorus Chemistry*, Marcel Dekker; New York, 1992.

3 (a) S.B. Hang, T.S. Mullins, H. Shim and F.M. Raushal, *Biochemistry,* 1997, **36**, 9022; (b) M.M. Berggren, L.A. Burns, R.T. Abraham, G. Powis, *Cancer Res.,* 1993, **53**, 1862; (c) X.D. Cao, E.J. Moran, D. Siev, A. Lio, C. Ohashi and A.M.M. Mjalli, *Bioorg. Med. Chem. Lett.*, 1995, **5**, 2953; (d) A. Caseli, G. Ciamici, G. Manao, G. Moneti, L. Pazzagli, G. Cappugi and G. Rammponi, *J. Biol. Chem.,* 1994, **269**, 24878.

4 (a) J.K. Stowell and T.S. Widlanski, *J. Org. Chem.,* 1995, **60**, 6930; (b) J.K. Myers, J.D. Cohen and T.S. Widlanski, *J. Am. Chem. Soc.,* 1995, **117**, 11049.; (c) T.S. Widlanski, J.K. Myer, B. Stec, K.M. Holtz and E.R. Kantroewitz, *Chem. Biol.* 1997, **4**, 489.

5 F. Maurer, H.J. Riebel, I. Hammann, W. Behrenz and B. Homeyer, Ger. Offen. 2533601, 1977; *Chem. Abstr.,* 1977, **87**, 17324.

6 Z.V. Molodykh, I.A. Aleksandrova, R.U. Belyalov, T.K. Gazizor and V.S. Reznik, *Khim.-Farm. Zh.,* 1990, **24**, 136. *Chem. Abstr.,* 1990, **113**, 20789.

7 C. Despax and J. Navech, *Tetrahedron Lett.,* 1990, **31**, 4471.

8 G. Trishin Yu, R.N. Burangulova, I.V. Konovalova, L.A. Burnaeva and G.S. Akimova, *Dokl. Akad. Nauk.,* 1989, **304**, 625; *Chem. Abstr.,* 1990, **112**, 35988.

9 (a) H.H. Wasserman and D. Cohen, *J. Am. Chem. Soc.,* 1960, **82**, 4435; (b) H.H. Wasserman and D. Cohen, *J. Org. Chem.,* 1964, **29**, 1817.

10 R. Hua and M. Tanaka, *Chem. Lett.,* 1998, 431.

11 A.-Y. Peng and Y.-X. Ding, *Synthesis,* 2003, 205.

12 (a) H.J. Reich, *Acc. Chem. Res*., 1979, **12**, 22; (b) D. Liotta, *Acc. Chem. Res*.; 1984, **17**, 28; (c) K.C. Nicolaou and N.A. Petasis, *Selenium in Natural Product Synthesis*, CIS: Philadelphia, 1984; (d) C. Paulmier, Ed.; *Selenium Reagents and Intermediates in Organic Synthesis*, Pergamon Press: Oxford, 1986; (e) T.G. Back, *Organoselenium Chemistry*, Oxford University Press: Oxford**,** 1999; (f) T. Wirth, *Organoselenium Chemistry*, Springer: Berlin, 2000.

13 For some recent selected examples on organoselenium, see: (a) N. Devan, P.R. Sirdhar, K.R. Prabhu and S. Chandrasekaran, *J. Org. Chem.,* 2002, **67**, 9417; (b) S.S. Khokhar and T. Wirth, *Angew. Chem., Int. Ed.,* 2004, **43**, 631; (c) G. Pandey and S.R. Gadre, *Acc. Chem. Res.,* 2004, **37**, 201.

14 (a) P.A. Bartlett and P.M. Chouinard, *J. Org. Chem.,* 1983, **48**, 3854; (b) T.-Q. Chen and M.M. Greenberg, *J. Am. Chem. Soc*., 1998, **120**, 3815.

15 A. Krief, *Tetrahedron,* 1980, **36**, 2531.

16 For some recent selected examples for preparation of tetrahydrofuran derivatives using phenyl β-hydroxyalkyl selenides, see: (a) S. Berlin, C. Ericsson and L. Engman, *J. Org. Chem.* 2003, **68**, 8386; (b) M. Tiecco, L. Testaferri, L. Bagnoli, V. Purgatorio, A. Temperini, F. Marini and C. Santi, *Tetrahedron: Asymm.,* 2004, **15**, 405.

17 For some recent selected examples, seen: (a) J.H. Rigby, U.S.M. Maharoof and M.E. Mateo, *J. Am. Chem. Soc.,* 2000, **122**, 6624; (b) H. Azuma, S. Tamagaki and K. Ogino, *J. Org. Chem.,* 2000, **65**, 3538; (c) T.D. Bagul, G. Lakshmaiah, T. Kawabata and K. Fuji, *Org. Lett.,* 2002, **4**, 249.

18 O. Mitsunobu, *Synthesis,* 1981, 1.

19 (a) S.-R. Sheng, X.-L. Liu, Q. Xu and C.-S. Song, *Synthesis,* 2003, 2763; (b) S.-R. Sheng, X.-L. Liu, X.-C. Wang, Q. Xin and C.-S. Song, *Synthesis* 2004, 2833; (c) X.-L. Liu, S.-R. Sheng, Q.-Y. Wang, W.-K. Sun, Q. Xin and H.-Y. Ao, *J. Chem. Res(S)*. 2006, 118.

20 (a) W.H.H. Gnther, *J. Org. Chem.,* 1966, **31**, 1202; (b) K.B. Sharpless and R.F. Lauer, *J. Am. Chem. Soc.,* 1972, **94**, 5115; (c) J. Remion, W. Dumont and A. Krief, *Tetrahedron Lett.,* 1976, **17**, 1385; (d) L. Engman and V. Gupta, *J. Org. Chem.,* 1997, **62**, 157.

21 R. Rabinowitz, *J. Am. Chem. Soc.,* 1960, **82**, 4564.

22 B.C. Saunders, G.J. Stacey, F. Wild and I.G.E. Wilding, *J. Chem. Soc.,* 1948, 699.

23 (a) P. Tavs, *Chem. Ber.*, 1970, **103**, 2428; (b) R.C. Grabiak, J.A. Miles and G.M. Schwenzer, *Phosphorus Sulfur Relat. Elem.,* 1980, **9**, 197.

24 T. Hirao, T. Masunaga, Y. Ohshiro and T. Agawa, *Synthesis*, 1981, 56.