A Simplified Preparation of Vinyl Sulfides, Selenides and Tellurides by a Wittig-Type Reaction[1]

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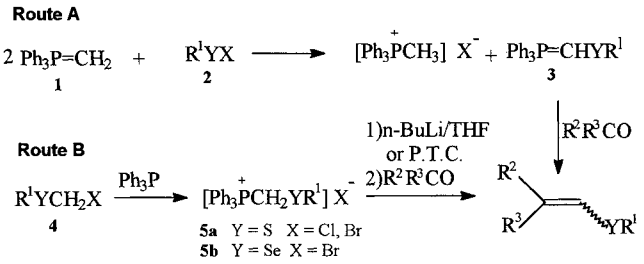
The preparation of several vinyl sulfides, selenides and tellurides by Wittig-type reaction in a one-pot procedure is described. The chalcogenyl triphenylphosphoranes **3** are formed "in situ" by the reaction of chloromethyl phenyl chalcogenide, potassium *tert*-butoxide and triphenylphosphine. Reaction of **3** with carbonyl compounds affords the vinyl chalcogenides **6–9** with preferential *Z*-configuration.

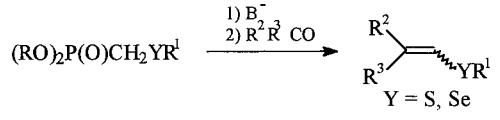
Considerable efforts have been directed to extend the Wittig and Horner–Wadsworth reaction to the preparation of α-metal and non-metal substituted olefins.[2] Important classes of such substituted olefins are vinyl sulfides,[3] selenides[4] and tellurides[5] which have found varied applications in organic synthesis. The appropriate α-substituted phosphonium salts or phosphonates are the obvious starting materials for these reactions.

The chalcogenophosphoranes **3** (Y = S, Se) are usually prepared by transylidation between an alkylidene triphenylphosphorane **1** (2 equiv) and a sulfenyl[6] or selenenyl[7] halide **2** (Route A) or by treatment of the corresponding thio[8] or seleno[7] phosphonium salts **5** with an appropriate base (Route B) (Scheme 1).



Scheme 1

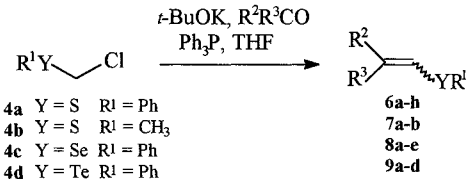
Thio- and selenophosphonates have also been exploited as reagents for the synthesis of vinyl sulfides[9,10] and selenides[11] (Scheme 2).



Scheme 2

The use of phase-transfer catalysts[12,13] or ultrasound[14] has been found to improve the yield of these reactions. Recently the preparation of *Z*[15]- and *E*[16]- vinyl tellurides by Horner/Wittig-type reactions was reported.

Herein we describe our results on the preparation of vinyl sulfides **6a–h** and **7a–b**, selenides **8a–e** and tellurides **9a–d** based on a very convenient one-pot procedure. The olefination reaction was performed by the addition of *t*-BuOK to a solution of chloromethylchalcogenide **4a–d** and triphenylphosphine in THF followed by addition of an aldehyde or ketone (Scheme 3).



6 - 9	R^2	R^3	6 - 9	R^2	R^3
a	C_6H_5	H	e	4-ClC_6H_4	H
b	2-Furyl	H	f	$CH_3CH_2CH_2$	H
c	4-$NO_2C_6H_4$	H	g	*i*-propyl	H
d	4-MeC_6H_4	H	h	-$CH_2(CH_2)_3CH_2$-	

Scheme 3

This method overcomes the prior two-step procedure for the vinyl sulfides or selenides via phosphonium salts **5a–b** which were prepared first from **4** and Ph_3P lowering the overall yield. The reactions described here are performed very easily by simple mixing of all the reagents at room temperature giving the expected vinylic chalcogenides in good yields (Table 1). Our method employs in all cases the chloro derivatives **4a–d** while the bromo derivative was used in the quaternization reaction to give the seleno compounds of type **5b**, because the chloro analogue does not react. On the other hand, quaternization using the chloro or bromo sulfides results in the formation of **5a** in good yields (Scheme 1) but similar reactions to obtain telluro analogs have not been described to date.

Although our reactions seem to be similar to those described to occur via transylidation or quaternization we believe that the mechanisms involved to form the chalcogenotriphenylphosphoranes are different in all three cases. In our reactions the first step probably involves the α-elimination of HCl in compounds **4a–d** with *t*-BuOK to form the corresponding α-chalcogenocarbenes[17] which in the presence of triphenylphosphine results in the formation of the corresponding chalcogenophosphoranes. The need for a second equivalent of *t*-BuOK was established experimentally since better yields are obtained. This additional equivalent probably could be responsible for shifting an equilibrium between *t*-BuOH and $R^1YCH = PPh_3$ for complete formation of the desired phosphoranes. In the same way, it was experimentally observed that yields were improved when 1.5 equivalents of Ph_3P were used instead 1.0 equivalent. However, theoretically only one equivalent of chalcogenophosphorane

Table 1. Vinylic Chalcogenides **6–9** Prepared

Product	Yield[a] (%)	Time (h)	mp (°C) or bp (°C)/Torr found	mp (°C) or bp (°C)/Torr reported	^{1}H NMR ($CDCl_3$/TMS) δ, J (Hz)	Ratio of E/Z-Isomers[b]	MS (m/z)
6a	84	0.5	122–125/ 0.15	102–103/ 0.05[13]	6.32 (d, 1H, *Z*, J = 11.2), 6.49 (d, 1H, J = 11.2), 6.66 (d, 1H, *E*, J = 15.2), 6.9 (d, 1H, *E*, J = 15.2), 7.1–7.8 (m, 10H)	30 : 70	212 (M^+)
6b	73	0.5	oil	–[c]	6.14–6.54 (m, 3H), 6.84 (d, 1H, J = 14.8), 7.21–7.44 (m, 6H)	40 : 60	202 (M^+)
6c	80	0.6	67–69	–[c]	6.41 (d, 1H, J = 15.2), 6.5–6.9 (m, 1H), 7.1–7.7 (m, 7H), 8.0–8.23 (m, 2H)	50 : 50	257 (M^+)
6d	65	0.6	oil	–[c]	2.22, 2.26 (2s, 3H), 6.30 (d, 1H, J = 11.2), 6.49 (d, 1H, J = 11.2), 6.58 (d, 1H, J = 15.2), 6.78 (d, 1H, J = 15.2), 7.0–7.3 (m, 6H), 7.4–7.6 (m, 2H)	25 : 75	226 (M^+)
6e	73	0.6	43–45	–[c]	6.48 (s, 2H, *Z*), 6.55 (d, 1H, J = 15.2), 6.86 (d, 1H, J = 15.2), 7.2–7.5 (m, 9H)	29 : 71	246 (M^+)
6f	55	2.0	116–119/ 0.15	–[c]	0.94 (t, 3H, J = 7.2), 1.46 (sext, 2H, J = 7.2), 2.17 (quint, 2H, J = 7.2), 5.7–6.3 (m, 2H), 7.1–7.4 (m, 5H)	25 : 75	178 (M^+)
6g	46	2.0	112–116/ 0.15	–[c]	0.96 (d, 6H, J = 7.2), 2.2–2.6 (m, 1H), 5.7–6.2 (m, 2H), 7.1–7.3 (m, 5H)	76 : 24	178 (M^+)
6h	51	3.0	122–126/ 0.15	133/ 1.1[25]	1.3–1.7 (m, 6H), 2.1–2.5 (m, 4H), 5.84 (s, 1H), 7.0–7.5 (m, 5H)	–	204 (M^+)
7a	62	0.5	61–64/ 0.15	85–86/ 1.5[9]	2.28, 2.30 (2s, 3H), 6.05 (d, 1H, J = 10.4), 6.16 (d, 1H, J = 15.2), 6.32 (d, 1H, J = 10.4), 6.65 (d, 1H, J = 15.2), 7.1–7.5 (m, 5H)	36 : 64	150 (M^+)
7b	71	0.5	oil	–[c]	*E*: 2.33 (s, 3H), 6.08 (d, 1H, J = 3.2), 6.16 (d, 1H, J = 15.2), 6.33 (dd, 1H, J = 3.2, 1.6), 6.75 (d, 1H, J = 15.2), 7.28 (d, 1H, J = 1.6), *Z*: 6.0–6.3 (m, 2H), 6.44 (br s, 2H), 7.3–7.4 (m, 1H)	61 : 39	140 (M^+)
8a	75	0.5	123–126/ 0.15	100–105/ 0.05[11]	6.6–7.0 (m, 2H), 7.1–7.7 (m, 10H)	51 : 49	260 (M + 1)
8b	69	0.5	oil	–[c]	6.1–6.2 (m, 1H), 6.2–6.5 (m, 2H), 6.6–6.8 (m, 1H), 7.0–7.6 (m, 6H)	39 : 61	250 (M + 1)
8c	75	0.6	76–79	67–76[11]	6.66 (d, 1H, J = 15.8), 6.9–7.7 (m, 8H), 8.08 (d, 2H, J = 8.8)	40 : 60	305 (M + 1)
8d	63	0.6	118–120/ 0.15	122/ 0.01[11]	2.22, 2.26 (2s, 3H), 6.55 (d, 1H, J = 9.6), 6.7–7.0 (m, 2H), 7.03–7.6 (m, 9H)	40 : 60	273 (M^+)
8e	72	0.6	73–75	–[c]	6.77–6.93 (m, 2H), 7.11–7.33 (m, 7H), 7.54–7.59 (m, 2H)	22 : 78	294 (M^+)
9a	45	0.6	41–43	43–44[26]	7.08 (d, 1H, J = 10.6), 7.17–7.35 (m, 8H), 7.47 (d, 1H, J = 10.6), 7.69–7.81 (m, 2H)	≥ 98 Z[d]	308 (M + 1)
9b	44	0.6	49–52	–[c]	6.29–6.44 (m, 2H), 6.85 (d, < 1H, J = 16, *E*), 6.98 (d, 1H, J = 10.2), 7.1–7.4 (m, 3H), 7.48–7.85 (m, 3H)	7 : 93	298 (M + 1)
9c	35	0.6	100–102	–[c]	6.94 (d, 1H, J = 16.6), 7.2–7.7 (m, 7H), 7.8–8.1 (m, 2H), 8.22 (d, 2H, J = 8)	21 : 79	354 (M + 2)
9d	34	0.6	52–54	54.5–55.5[27]	2.31 (s, 3H), 6.9 (d, 1H, J = 10.4), 7.0–7.25 (m, 7H), 7.33 (d, 1H, J = 10.4), 7.63–7.75 (m, 2H)	6 : 94	322 (M + 1)

[a] Yields refer to products purified by column chromatography.
[b] Determined by GC or ^{1}H NMR.
[c] Satisfactory microanalyses obtained: C ± 0.39, H ± 0.21. Exception: **6b** C + 2.46; **8b** C − 1.55.
[d] Only the *Z* isomer could be detected by ^{1}H NMR and ^{13}C NMR.

is formed since the chloromethylchalcogenides **4a–d** are the limiting reagents. Although excess of base could promote undesired reactions with enolizable substrates, reactions of **4a** with isobutyraldehyde, butyraldehyde or cyclohexanone were successful and result in the formation of the corresponding vinyl sulfides **6f–h** in 46–73% yields (Table 1).

The stereochemistry of the products obtained in these olefination reactions shows an isomeric Z/E-mixture (established by comparative GC with authentic samples[7,11,14] and ^{1}H NMR spectroscopy). The *Z*-isomer was detected as the major component in the mixture, in accordance with the known stereochemical course of Wittig olefinations under lithium salt free conditions.[18] The solvent of choice for sulfur and selenium species was THF since lower yields are obtained by using DMF or HMPA or a mixture of these solvents, as shown in Table 2. Otherwise, in the case of tellurium derivatives, very low yields were obtained with THF which were improved using a mixture of THF/DMF (3:1).

At the beginning of the present study, there had been no reports on the preparation of vinyl tellurides by a Wittig route. However, very recently Oh et al.[16] described the reaction of tellurium phosphonates with aromatic aldehydes giving *E*-vinyl tellurides, and we have reported their preparation with a *Z*-preferential stereochemistry.[15] Our present results are complementary to the precedent ones, since *Z*-vinyl tellurides are preferentially or exclu-

Table 2. Preparation of **6a** and **8a** in Different Solvents

Product	Solvent	Yield[a] (%)
6a	THF	84
6a	DMF	61
6a	THF/DMF (3 : 1)	66
6a	HMPA	58
6a	THF/HMPA (3 : 1)	70
8a	THF	75
8a	DMF	59
8a	THF/DMF (3 : 1)	64
8a	HMPA	57
8a	THF/HMPA (3 : 1)	65

[a] Yields determined for a reaction time of 35 min at r.t., using chloromethyl phenyl chalcogenide (1.0 mmol), Ph_3P (1.5 mmol), *t*-BuOK (2.0 mmol) and benzaldehyde (1.5 mmol) in the specified solvent (4 mL).

sively produced. For example, in the case of β-styryl phenyl telluride **9a**, the exclusive *Z*-isomer could be identified by 200 MHz ^1H NMR spectra, where only two doublets could be detected at $\delta = 7.08$ and 7.47 with $J = 10.6$ Hz, characteristic of the *Z*-isomer.[19] The *E*-isomer has been described[16] as exhibiting two doublets at $\delta = 7.20$ and 7.64 with $J = 16.6$ Hz.

The employed methods to prepare the chloromethyl chalcogenides **4a–d** and the use of them in the present Wittig-type reaction have several advantages. For example **4a** is commercially available or can be easily obtained in high yield by the reaction of thioanisole with sulfuryl chloride. Compound **4b** is obtained in the same way using dimethyl sulfide, while **4c** and **4d** are prepared by reaction of the corresponding phenyl chalcogenolate anions with CH_2Cl_2 (experimental section). All these compounds can be prepared in large scale and are more stable than phenyl chalcogenenyl halides, which are used in transylidation and in tedious reactions with diazo compounds to obtain **4c** as precursor of **5b** accordingly with previous reports.[7] However, it must be considered that PhSeCl is commercially available and other compounds such as PhSeBr, PhTeBr and PhSCl are readily generated and used in situ.

Compound **4d** was described in the literature as an unstable compound.[20] However, we purified **4d** by distillation in a Kugelrohr apparatus and observed that it can be stored in the freezer for several days without decomposition.

These results clearly demonstrate that our modified procedure for the synthesis of vinyl chalcogenides is a valuable improvement over the existing methods due to the simple one-pot experimental manipulations and the superior selectivity in the formation of *Z*-isomers.

All reagents were of commercial quality. Carbonyl compounds were purchased from Aldrich Chemical Co. or Merck and were distilled before use. SO_2Cl_2 was purified by passing over a column of basic alumina followed by distillation. All products were purified by column chromatography (silica gel Merck 230–400 mesh). Melting points (uncorrected) were determined with a Kofler melting point apparatus. Mass spectra were recorded on a HP GC/MS 5988A. Microanalyses were obtained using a Perkin-Elmer 2400 apparatus. IR spectra were recorded on a FT-IR BOMEM spectrophotometer and ^1H NMR spectra on a Bruker AC-80 (80 MHz) or Bruker AC-200 (200 MHz) spectrometer, with TMS as internal standard and CCl_4 or $CDCl_3$ as the solvent.

Chloromethyl phenyl sulfide **(4a)**,[21] chloromethyl methyl sulfide **(4b)**,[22] chloromethyl phenyl selenide **(4c)**[23,24] and chloromethyl phenyl telluride **(4d)**[20] were prepared according to literature methods.

Vinylic Sulfides, Selenides and Tellurides 6–9; General Procedure:
In a two-necked 15 mL round bottom flask, equipped with a magnetic stirrer, containing a solution of chloromethyl phenyl chalcogenide (1.0 mmol) and Ph_3P (0.39 g, 15 mmol) in anhyd THF (4 mL for vinyl sulfides and selenides, or a mixture of THF/DMF, 3 + 1 mL for vinyl tellurides) under N_2, was added in portions *t*-BuOK (0.22 g, 2.0 mmol). The reaction mixture became yellow and after 5 min the carbonyl compound (1.5 mmol) was added. The solution became milky and the mixture was stirred at r.t. (at reflux for vinyl sulfides derived from aliphatic aldehydes and cyclohexanone) for the time given in Table 2. The reaction was quenched with water (30 mL) and the product extracted with EtOAc (2 × 20 mL). The combined organic layers were dried ($MgSO_4$), filtered and the solvent removed. The residue was purified by column chromatography (silica gel; hexane). When possible, the products were distilled in a Kugelrohr apparatus (see Table 2).

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