

Preparation and Reactivity of Chalcogenyl Phosphonates and Phosphane Oxides

Claudio C. Silveira,^{*,[a]} Francieli Rinaldi,^[a] and Rafael C. Guadagnin^[a]

Keywords: Horner–Wittig reaction / Chalcogens / Phosphane oxides / Selenium / Tellurium

The preparation of new bis(diphenylphosphinoyl)methyl sulfides, selenides, and tellurides is described by the reaction of (diphenylphosphinoyl)methyl *p*-toluenesulfonate with sodium chalcogenides. The title compounds are subjected to Horner–Wittig-type reactions with aldehydes and ketones to give symmetrical divinyl sulfides, selenides, and tellurides

with preferential (*E*) stereochemistry. Unsymmetrical divinyl sulfides can be prepared by the use of an appropriate carbonyl compound.

(© Wiley-VCH Verlag GmbH & Co. KGaA, 69451 Weinheim, Germany, 2007)

Introduction

Organochalcogenium compounds have recently attained remarkable development as synthetic reagents and intermediates; they are not only the subject of many review articles^[1] but books as well.^[2] Among the many classes of organochalcogenium compounds, vinylic chalcogenides exhibit a peculiar role.^[3] Several methods for the synthesis of vinylic chalcogenides are known and the Wittig or Horner–Wittig reactions are among the most useful ones.^[4] We^[5] and others^[6] recently reported convenient methods for the synthesis of vinylic selenides, vinylic tellurides, and also vinylic sulfides by Wittig or Horner–Wittig reactions.

From the many applications of vinyl selenides and vinyl sulfides, the nickel-catalyzed coupling reaction with Grignard reagents to give the corresponding cross-coupled products has been described.^[7] A chemoselective coupling reaction was described by the reaction of (*E*)- and (*Z*)-(phenylthio)ethenyl methyl selenides with Grignard reagents, catalyzed by Ni^{II} species, in which only the selenium organyl was removed. Stereospecific carbon–selenium bond cleavage can be achieved by choosing the appropriate Ni catalyst.^[8] The coupling of vinylic selenides with trimethylsilylmagnesium chloride by NiCl₂(Ph₃P)₂ or PdCl₂(Ph₃P)₂ catalysis has also been applied to the synthesis of allylsilanes.^[9] However, in all these methods, when the coupling reaction is performed, one of the two organic moieties linked to the chalcogen atom, which is usually a phenyl or a methyl group, is lost. To address this problem, we envisioned that by using divinyl selenides in these coupling reactions, both organyls linked to selenium could be trans-

ferred.^[5d] The synthesis of divinyl selenides by the Wittig–Horner reaction was recently studied and described by the reaction of the corresponding selenium bis(phosphonate) with aromatic aldehydes.^[5d] In the case of vinylic tellurides, the most useful methods are Pd-catalyzed homocoupling^[10] and cross-coupling reactions,^[11] Ni^{II}-catalyzed cross-coupling reactions with alkynes^[12a] and metal acetylides,^[12b] and carbonylation in the presence of Pd^{II} salts leading to carbonylic acids.^[13,14] Vinyl tellurides are especially useful in transmetalation reactions. Their treatment with lithium,^[15] Li/Ce,^[15a] Li/Zn,^[16] Zn,^[17,18] sodium,^[19] calcium,^[19] or Grignard reagents,^[20] followed by the capture of the vinyl metals with electrophiles, occurs with retention of the carbon–carbon bond geometry. In addition, higher order vinylcuprates [vinylCu(R)CNLi₂] can be accessed upon transmetalation of vinyl tellurides with higher order cyanocuprates, and they can undergo 1,4-addition to enones,^[21] epoxides,^[21a,22] and bromoalkynes.^[23] Substitution of the tellurium moieties by methyl or alkyl groups is achieved upon treatment with Me₂CuLi,^[15d] with Grignard reagents,^[24] magnesium higher order cuprates,^[25] and alkyl- and alkynylzinc reagents.^[26]

A straightforward method for the preparation of symmetrical divinyl tellurides is based on the hydrotelluration of acetylenes with the system Te/NaBH₄/EtOH/THF/NaOH (aqueous).^[27] This method, however, produces predominantly (*Z*) adducts, but it is efficient only with acetylenes conjugated to aryl groups, C=C bonds, or other electron-withdrawing groups. In contrast, alkyl acetylenes are fairly unreactive. Another method recently described for the preparation of symmetrical divinyl tellurides employs aryl-tellurophosphoranes derived from bis(triphenylmethylphosphonium) halotellurates.^[5b]

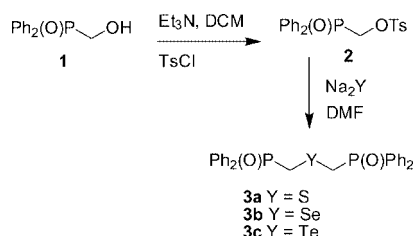
In light of the above comments it is of interest to develop practical stereoselective synthetic methods for symmetrical and unsymmetrical divinyl chalcogenides with the aim to

[a] Departamento de Química, Universidade Federal de Santa Maria, Caixa Postal 5001 Campus, 97105-900 Santa Maria, RS, Brazil
Fax: +55-55-3220-8754
E-mail: silveira@quimica.ufsm.br

use them in the construction of olefins with defined stereochemistries and to attain easy access to vinyl–metal species. Particularly interesting is the possibility that both organyls linked to the chalcogenium atom in divinyl chalcogenides could be used.

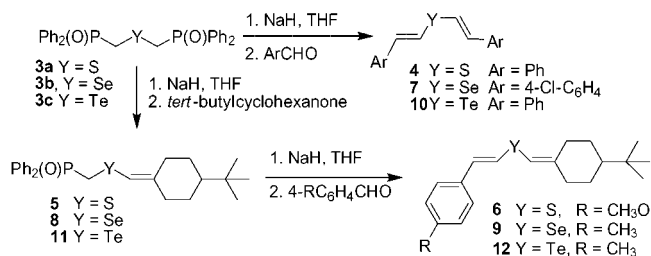
Results and Discussion

Here we describe our results obtained in the convenient preparation of (tosylmethyl)diphenylphosphane oxide **2**^[28,29] from **1**, and its conversion into bis(methyldiphenylphosphane oxide) sulfide **3a**, selenide **3b**, and telluride **3c** by reaction with Na₂Y (Y = S, Se, Te) in DMF (Scheme 1).



Scheme 1.

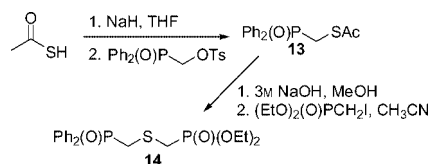
Compound **1** was prepared by the reaction of diphenylphosphane^[30] with Na or Li, in THF, followed by the addition of *p*-formaldehyde at -40°C . After the reaction was complete, H₂O₂ (30% vol) was slowly added, at 0°C to give **1** in 81% isolated yield. Next, treatment of hydroxylmethyl-diphenylphosphane oxide **1** with base (Et₃N) and TsCl in CH₂Cl₂ at 0°C furnished the corresponding tosylate **2** in 96% isolated yield. This interesting tosylate was prepared previously in THF^[31] and in pyridine.^[32] To our purposes, tosylate **2** can be conveniently converted to sulfide **3a**, selenide **3b**, or telluride **3c** by treatment with sodium chalcogenolates in DMF. Compounds **3a–c** are very interesting species, as they combine three active sites for metal binding, which are the chalcogen atom and the two diphenylphosphoryl groups. We disclose here their use in Horner–Wittig-type reactions, which could furnish the corresponding divinyl chalcogenides according to Scheme 2. Thus, treatment of **3a** with an excess amount of base (NaH) and 3 equiv. of benzaldehyde furnished the corresponding bis(styryl) sulfide in 85% yield. We performed some reactions with KH as the base, but no improvements in the yield or stereoselectivity of the reaction was observed. We next observed that in the reaction of **3a** with ketones, which are less reactive in Wittig-type reactions, one can selectively perform the reaction at one side of the substrate and vinylic sulfide **5** can be prepared. Sulfide **5** can be isolated and purified and subsequently reacted with a different carbonyl compound, such as *p*-anisaldehyde to give **6**, which allows easy entry to unsymmetrical divinyl sulfides (Scheme 2). Similar reactions can be performed with selenide **3b** and telluride **3c** to give symmetrical selenide **7** and telluride **10** and unsymmetrical selenide **9** and telluride **12**, respectively.



Scheme 2.

In all examples, a high preference for the (*E/E*) isomers could be detected by ¹H and ¹³C NMR spectroscopy, which is in accordance with these one-step Horner–Wittig reactions of phosphane oxides, usually (*E*) selective.^[33] For example, in the synthesis of vinyl sulfides^[34] or vinyl fluorides,^[31] the diastereomeric ratio was 3:1 or lower. Pure (*E*) or (*Z*) alkenes would be accessible by the two-step Horner–Wittig strategy.^[33] We were also able to obtain the pure (*E*) isomer by successive washings with petroleum ether.

An interesting mixed phosphorus sulfide can be prepared by a convenient choice of adequate starting materials. Thus, phosphonoxide **13**^[35] can be prepared from CH₃COSH by treatment with NaH followed by reaction with tosylate **2**. Basic hydrolysis of **13** in MeOH and reaction with iodo-methyl (diethyl)phosphonate in CH₃CN furnishes **14** (Scheme 3). Preliminary studies on the reactivity of **14** with NaH and cyclic ketones showed a small preference for the mono Horner–Wittig reaction to occur at the diphenylphosphane oxide side (ca. 3:1). In the next step, reaction of the intermediate with aromatic aldehydes furnishes unsymmetrical divinyl sulfides in a reaction closely related to the one described in Scheme 2 to give compound **6**.



Scheme 3.

Conclusions

We described a convenient method for the preparation of bis[(diphenylphosphinoyl)methyl] sulfide, selenide, and telluride by the reaction of (diphenylphosphinoyl)methyl *p*-toluenesulfonate with sodium sulfide, selenide, and telluride, respectively. The bis[(diphenylphosphinoyl)methyl] chalcogenides were subjected to Horner–Wittig reactions with arenecarbaldehydes and NaH as base to give symmetrical divinyl sulfides, selenides, and tellurides, with preferential (*E*) stereochemistry. Unsymmetrical divinyl sulfides can be prepared by the reaction with ketones followed by arenecarbaldehydes.

Experimental Section

(Diphenylphosphinoyl)methanol (1): Diphenylphosphane^[30] (5.59 g, 30 mmol) was added to a flask containing Na metal (0.80 g, 35 mmol; cut into small pieces) in THF (60 mL) under an atmosphere of argon, at 0 °C, and the reaction became reddish. Stirring was maintained for an additional 20 min and then at room temp. for 24 h. The reaction was then cooled to –40 °C and paraformaldehyde (0.99 g) was added. The temperature was slowly raised to room temp. and stirred for another 24 h. Then, H₂O (30 mL) was added slowly, and the reaction was stirred for another 20 min and neutralized to pH 7 with HCl (3 M). The organic phase was separated, H₂O₂ (30% vol, ca 6 mL) was added dropwise at 0 °C. The reaction was followed by TLC and after 2 h H₂O was added. The solution was extracted with ethyl acetate (2 × 60 mL), and the combined organic layers were washed with brine and dried (MgSO₄). After filtration, the solvents were removed under reduced pressure, and the residue was purified by recrystallization (ethyl acetate/hexanes, 1:9). Yield: 83%. M.p. 136–137 °C. ¹H NMR (400 MHz, CDCl₃): δ = 4.40 (s, 2 H), 5.82 (s, 1 H), 7.42–7.50 (m, 6 H), 7.72–7.77 (m, 4 H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 60.93 (d, *J*_{PC} = 84.06 Hz), 128.43 (d, *J*_{PC} = 11.30 Hz), 130.45 (d, *J*_{PC} = 96.07 Hz), 131.21 (d, *J*_{PC} = 9.18 Hz), 131.90 (d, *J*_{PC} = 2.82 Hz) ppm.

(Diphenylphosphinoyl)methyl *p*-Toluenesulfonate (2): To a solution of (diphenylphosphinoyl) methanol **1** (4.64 g, 20 mmol) in CH₂Cl₂ (50 mL), under an atmosphere of argon, was added triethylamine (2.12 g, 21 mmol) dropwise at 0 °C. The reaction mixture was stirred 30 min at room temp., cooled to 0 °C, and *p*-tosyl chloride (4.34 g, 21 mmol) was added. The reaction was kept at 0 °C for 30 min and then 4 h at room temp. Water (50 mL) was added, and the mixture was extracted with CH₂Cl₂ (3 × 30 mL). The organic layer was dried (MgSO₄), and the solvent was removed under reduced pressure. The solid residue was recrystallized (CH₂Cl₂/Et₂O, 1:9) to afford colorless crystals. Yield: 96%. M.p. 124–125 °C (ref.^[31] 124–125 °C). ¹H NMR (400 MHz, CDCl₃): δ = 2.42 (s, 3 H), 4.62 (d, *J*_{PH} = 7.03 Hz, 2 H), 7.26 (d, *J* = 7.78 Hz, 2 H), 7.48–7.62 (m, 8 H), 7.70–7.74 (m, 4 H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 21.49, 64.60 (d, *J*_{PC} = 82.05 Hz), 127.95, 128.63 (d, *J*_{PC} = 13.04 Hz), 128.84 (d, *J*_{PC} = 103.84 Hz), 129.83, 130.93, 131.28 (d, *J*_{PC} = 9.97 Hz), 132.66 (d, *J*_{PC} = 3.07 Hz), 145.39 ppm.

Bis[(diphenylphosphinoyl)methyl] Sulfide (3a): To a solution of tosylmethylidiphenylphosphane oxide **2** (3.86 g, 10 mmol) in dry DMF (30 mL), under an atmosphere of argon at 0 °C, was added an excess amount of Na₂S (0.780 g, 10 mmol) in small portions. The reaction mixture was heated at 60 °C for 90 min and then water (50 mL) was added, and the mixture was extracted with ethyl acetate (4 × 50 mL). The combined organic layers were washed with water (2 × 100 mL) and brine (100 mL). The organic layer was dried (MgSO₄), and the solvent was removed under reduced pressure. The solid residue was recrystallized (CH₂Cl₂/Et₂O, 1:9) to give **3a**. Yield: 81%. M.p. 149–152 °C. ¹H NMR (400 MHz, CDCl₃): δ = 3.59 (d, *J*_{PH} = 6.19 Hz, 4 H), 7.41–7.53 (m, 12 H), 7.70–7.79 (m, 8 H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 29.77 (d, *J*_{PC} = 69.40 Hz), 128.53 (d, *J*_{PC} = 11.60 Hz), 131.01 (d, *J*_{PC} = 9.70 Hz), 131.39 (d, *J*_{PC} = 100.05 Hz), 131.98 (d, *J*_{PC} = 1.50 Hz) ppm. IR (KBr): ν̄ = 1180 (P=O), 1367, 1436, 2896 cm^{–1}. MS: *m/z* (%) = 462 (6) [M]⁺, 217 (21), 216 (22), 215 (100), 201 (28), 183 (15), 125 (11), 91 (51), 77 (37), 51 (21), 47 (31). C₂₆H₂₄O₂P₂S (462.48): calcd. C 67.21, H 5.51; found C 67.52, H 5.23.

Bis[(diphenylphosphinoyl)methyl] Selenide (3b): To a solution of tosylmethylidiphenylphosphane oxide **2** (3.86 g, 10 mmol) in dry DMF (20 mL), under an atmosphere of argon at 0 °C, was added Na₂Se

(6 mmol; prepared as below) in small portions.^[36] The reaction mixture was stirred for 1 h at 0 °C, then another 4 h at room temp. After this, water (50 mL) was added, and the mixture was extracted with ethyl acetate (4 × 50 mL). The combined organic layers were washed with water (2 × 100 mL) and brine (100 mL). The organic layer was dried (MgSO₄), and the solvent was removed under reduced pressure. The residue was recrystallized (CH₂Cl₂/Et₂O, 1:9). Yield: 79%. M.p. 171–174 °C. ¹H NMR (200 MHz, CDCl₃): δ = 3.47 (d, *J*_{PH} = 5.73 Hz, 4 H), 7.27–7.56 (m, 12 H), 7.70–7.80 (m, 8 H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 19.35 (d, *J*_{PC} = 69.90 Hz), 128.36 (d, *J*_{PC} = 12.00 Hz), 130.80 (d, *J*_{PC} = 9.89 Hz), 131.73 (d, *J*_{PC} = 2.82 Hz), 132.07 (d, *J*_{PC} = 101.0 Hz) ppm. IR (KBr): ν̄ = 1193 (P=O), 1332, 1438, 2905 cm^{–1}. MS: *m/z* (%) = 510 (2) [M]⁺, 292 (34), 216 (18), 215 (100), 201 (30), 183 (19), 91 (54), 77 (45), 65 (10), 51 (28), 47 (35). HRMS (ESI): calcd. for C₂₆H₂₄NaO₂P₂Se [M + Na]⁺ 533.0314; found 533.0309.

Preparation of Na₂Se: Se (474 mg, 6 mmol) was added to a solution of THF (15 mL), Na (32 mg, 14 mmol), and naphthalene (256 mg, 2 mmol) under an atmosphere of argon. The mixture was heated at reflux for 3 h, and after the color of the solution turned yellow, DMF (15 mL) was added. THF was removed with a Dean–Stark apparatus by heating under a flow of argon, and the solution was then ready to use.

Bis[(diphenylphosphinoyl)methyl] Telluride (3c): To a solution of tosylmethylidiphenylphosphane oxide **2** (3.86 g, 10 mmol) in dry DMF (20 mL), under an atmosphere of argon at 0 °C was added Na₂Te (6 mmol, prepared from Te and NaH in DMF)^[2a] in small portions. The reaction mixture was stirred for 4 h at 50 °C and then water (50 mL) was added. The mixture was filtered through Celite, extracted with ethyl acetate (4 × 50 mL), and the combined organic layers were washed with water (2 × 100 mL) and brine (100 mL). The organic layer was dried (MgSO₄), and the solvent was removed under reduced pressure. The solid residue was recrystallized (CH₂Cl₂/Et₂O, 1:9). Yield: 71%. M.p. 159–162 °C. ¹H NMR (400 MHz, CDCl₃): δ = 3.46 (d, *J*_{PH} = 6.51 Hz), 7.41–7.52 (m, 12 H), 7.70–7.77 (m, 8 H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = –1.23 (d, *J*_{PC} = 68.24 Hz), 128.47 (d, *J*_{PC} = 12.27 Hz), 130.97 (d, *J*_{PC} = 9.97 Hz), 131.72 (d, *J*_{PC} = 3.07 Hz), 132.84 (d, *J*_{PC} = 101.21 Hz) ppm. IR (KBr): ν̄ = 1181 (P=O), 1437 cm^{–1}. MS: *m/z* (%) = 558 (2) [M – 2]⁺, 353 (65), 229 (39), 227 (25), 215 (60), 201 (86), 183 (28), 91 (29), 77 (100), 51 (66), 47 (44). HRMS (ESI): calcd. for C₂₆H₂₄NaO₂P₂Te [M + Na]⁺ 583.0211; found. 583.0219.

General Procedure for the Preparation of Divinyl Chalcogenides 4, 7, and 10: NaH (dry 95%; 51 mg, 2 mmol) was added to a solution of chalcogeno bis(phosphane oxide) (0.5 mmol) in THF (10 mL) at room temp. After 20 min, the appropriate carbonyl compound (1.5 mmol) was added, and the mixture was stirred for 3 h. A solution of saturated aqueous NH₄Cl was then added, and the mixture was extracted with ethyl acetate (20 mL). The organic layer was dried (MgSO₄), filtered, and removed under reduced pressure. The residue was purified by column chromatography (hexanes).

Bis(styryl) Sulfide (4): Yield: 85%. M.p. 40–42 °C. (*E/Z*), 7.2:1. Mixture of (*E/Z*) isomers: ¹H NMR (400 MHz, CDCl₃): δ = 6.46 (d, *J* = 10.8 Hz, 1 H), 6.59 (d, *J* = 10.8 Hz, 1 H), 6.67 (d, *J* = 15.6 Hz, 1 H), 6.82 (d, *J* = 15.6 Hz, 1 H) ppm. (*E/E*) Isomer: ¹H NMR (400 MHz, CDCl₃): δ = 6.68 (d, *J* = 15.6 Hz, 2 H), 6.85 (d, *J* = 15.6 Hz, 2 H), 7.20–7.39 (m, 10 H, arom) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 121.86, 125.90, 127.48, 128.64, 130.60, 136.43 ppm. IR (KBr): ν̄ = 942, 1444, 1567, 1595 cm^{–1}. GC–MS: *m/z* (%) = 238 (100) [M]⁺, 134 (32), 129 (33), 128 (40), 121 (77), 116 (56), 115 (85), 91 (74), 77 (85), 65 (32), 51 (69), 45 (33).

Bis(4-chlorostyryl) Selenide (7): Yield 70%. M.p. 121–123 °C. (*E/Z*), 7.7:1. Mixture of (*E/Z*) isomers: ^1H NMR (400 MHz, CDCl_3): δ = 6.79 (d, J = 10.3 Hz, 1 H), 6.96 (d, J = 10.3 Hz, 1 H), 7.09 (d, J = 15.81 Hz, 1 H) ppm. (*E/E*) Isomer: ^1H NMR (400 MHz, CDCl_3): δ = 6.82 (d, J = 15.8 Hz, 2 H), 7.12 (d, J = 15.8 Hz, 2 H), 7.25–7.34 (m, 10 H, arom) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ = 118.36, 127.12, 128.81, 133.33, 133.45, 135.26 ppm. IR (KBr): $\tilde{\nu}$ = 1100, 1174, 1400, 1488, 1586 cm^{-1} . GC–MS: m/z (%) = 354 (24) $[\text{M}]^+$, 274 (37), 239 (57), 204 (75), 182 (28), 125 (31), 101 (100), 75 (64), 51 (32).

Bis(styryl) Telluride (10): Yield: 78%. M.p. 50–52 °C. (*E/Z*), 6:1. Mixture of (*E/Z*) isomers: ^1H NMR (400 MHz, CDCl_3): δ = 7.11 (d, J = 10.5 Hz, 1 H), 7.14 (d, J = 16.82 Hz, 1 H), 7.46 (d, J = 16.82 Hz, 1 H), 7.51 (d, J = 10.5 Hz, 1 H) ppm. (*E/E*) Isomer: ^1H NMR (400 MHz, CDCl_3): δ = 7.16 (d, J = 16.56 Hz, 2 H), 7.50 (d, J = 16.56 Hz, 2 H), 7.22–7.39 (m, 10 H, arom) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ = 99.89, 126.02, 127.81, 128.53, 138.01, 143.07 ppm. IR (KBr): $\tilde{\nu}$ = 958, 1153, 1431, 1486, 1583, 1764, 1972 cm^{-1} . GC–MS: m/z (%) = 336 (11) $[\text{M}]^+$, 210 (100), 209 (17), 195 (21), 179 (13), 167 (27), 165 (14), 90 (21), 89 (30), 77 (44).

(4-*tert*-Butylcyclohexylidene)methyl (Diphenylphosphinoyl)methyl Sulfide (5): NaH (dry 95%; 51 mg, 2 mmol) was added to a solution of chalcogeno bis(phosphane oxide) **3a** (462 mg, 1 mmol) in THF (10 mL) at room temp. After 20 min, *tert*-butylcyclohexanone (170 mg, 1.1 mmol) was added. The reaction was stirred for 6 h at 65 °C (oil bath temperature), and a solution of saturated aqueous NH_4Cl was added. The mixture was then extracted with ethyl acetate (30 mL). The organic layer was dried (MgSO_4), filtered, and removed under reduced pressure. The residue was purified by column chromatography (CH_2Cl_2 /hexanes/ethyl acetate, 1:5:4) to give **5**. Yield 65%. M.p. 177–179 °C. ^1H NMR (200 MHz, CDCl_3): δ = 0.82 (s, 9 H), 0.86–1.16 (m, 3 H), 1.53–1.97 (m, 4 H), 2.13–2.20 (m, 1 H), 2.68–2.75 (m, 1 H), 3.39 (d, J_{PH} = 8.25 Hz, 2 H), 5.55 (s, 1 H), 7.42–7.59 (m, 6 H), 7.75–7.85 (m, 4 H) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ = 27.47, 27.55, 28.47, 29.82, 32.30, 32.46 (d, J_{PC} = 69.40 Hz), 35.94, 47.76, 113.58 (d, J_{PC} = 2.83 Hz), 128.43 (d, J_{PC} = 11.30 Hz), 128.46 (d, J_{PC} = 12.01 Hz), 131.22 (d, J_{PC} = 9.20 Hz), 131.29 (d, J_{PC} = 9.20 Hz), 131.78 (d, J_{PC} = 103.30 Hz), 131.56 (d, J_{PC} = 103.30 Hz), 131.96 (d, J_{PC} = 2.83 Hz), 144.34 ppm. IR (KBr): $\tilde{\nu}$ = 1192 (P=O), 1436, 1618 (C=C) cm^{-1} . MS: m/z (%) = 398 (1) $[\text{M}]^+$, 249 (8), 248 (10), 216 (48), 215 (100), 91 (10), 57 (12), 41 (15). $\text{C}_{24}\text{H}_{31}\text{OPS}$ (398.54): calcd. C 71.78, H 7.63; found C 72.33, H 7.84.

General Procedure for the Preparation of Unsymmetrical Divinyl Chalcogenides 6, 9, and 12: NaH (dry 95%; 25 mg, 1 mmol) was added to a solution of chalcogeno phosphane oxide **5**, **8**, or **11** (0.5 mmol) in THF (15 mL) at room temp. After 20 min, the appropriate aldehyde (0.75 mmol) was added. The reaction was stirred for 3 h at room temp., saturated aqueous NH_4Cl was added, and the mixture was extracted with ethyl acetate (20 mL). The organic layer was dried (MgSO_4) and filtered, and the solvent was removed under reduced pressure. The residue was purified by column chromatography (hexanes).

(4-*tert*-Butylcyclohexylidene)methyl (4-Methoxystyryl) Sulfide (6): Yield: 78%. M.p. 67–69 °C. (*Z/E*), 1:12. (*E*) Isomer: ^1H NMR (200 MHz, CDCl_3): δ = 0.86 (s, 9 H), 1.00–1.27 (m, 3 H), 1.75–1.92 (m, 3 H), 2.05–2.18 (m, 1 H), 2.36–2.46 (m, 1 H), 2.79–2.89 (m, 1 H), 3.79 (s, 3 H), 5.80 (s, 1 H), 6.43 (d, J = 15.34 Hz, 1 H), 6.59 (d, J = 15.34 Hz, 1 H), 6.83 (d, J = 8.89 Hz, 2 H), 6.59 (d, J = 8.89 Hz, 2 H) ppm. (*E*) Isomer: ^{13}C NMR (100 MHz, CDCl_3): δ = 27.54, 27.87, 28.86, 30.30, 32.40, 36.37, 47.90, 55.17, 111.05, 113.97, 121.76, 126.61, 126.66, 129.93, 146.10, 158.62 ppm. IR

(KBr): $\tilde{\nu}$ = 1255, 1462, 1568, 1606 cm^{-1} . GC–MS: m/z (%) = 317 (190) $[\text{M} + 1]^+$, 316 (81) $[\text{M}]^+$, 217 (25), 195 (77), 147 (25), 134 (82), 122 (19), 121 (100), 97 (30), 91 (19), 57 (60), 44 (27), 43 (35), 41 (37). $\text{C}_{20}\text{H}_{28}\text{OS}$ (316.51): calcd. C 75.90, H 8.92; found C 75.84, H 8.99.

(4-*tert*-Butylcyclohexylidene)methyl (4-Methylstyryl) Selenide (9): Yield: 79%. (*Z/E*), 1:16. (*E*) Isomer: ^1H NMR (200 MHz, CDCl_3): δ = 0.85 (s, 9 H), 1.01–1.22 (m, 3 H), 1.86–1.88 (m, 3 H), 2.09–2.16 (m, 1 H), 2.30 (s, 3 H), 2.44–2.48 (m, 1 H), 2.72–2.77 (m, 1 H), 6.01 (s, 1 H), 6.68 (d, J = 15.74 Hz, 1 H), 6.96 (d, J = 15.74 Hz, 1 H), 7.08 (d, J = 7.99 Hz, 2 H), 7.18 (d, J = 7.99 Hz, 2 H) ppm. (*E*) Isomer: ^{13}C NMR (100 MHz, CDCl_3): δ = 21.13, 27.56, 27.98, 28.88, 32.32, 32.38, 37.01, 47.85, 107.10, 110.31, 118.31, 125.56, 129.24, 131.60, 136.78, 148.08 ppm. GC–MS: m/z (%) = 348 (12) $[\text{M}]^+$, 346 (6), 267 (7), 197 (8), 142 (10), 131 (16), 115 (19), 105 (35), 79 (32), 57 (100), 41 (68). $\text{C}_{20}\text{H}_{28}\text{Se}$ (347.38): calcd. C 69.15, H 8.12. found C 69.30, H 8.21.

(4-*tert*-Butylcyclohexylidene)methyl (4-Methylstyryl) Telluride (12): Yield: 74%. (*Z/E*), 1:15. (*E*) Isomer: ^1H NMR (400 MHz, CDCl_3): δ = 0.86 (s, 9 H), 1.01–1.22 (m, 3 H), 1.83–1.90 (m, 3 H), 1.95–2.02 (m, 1 H), 2.20–2.27 (m, 1 H), 2.32 (s, 3 H), 2.50–2.56 (m, 2 H), 6.24 (s, 1 H), 6.97 (d, J = 16.59 Hz, 1 H), 7.10 (d, J = 7.99 Hz, 2 H), 7.20 (d, J = 7.99 Hz, 2 H), 7.28 (d, J = 16.59 Hz, 1 H) ppm. (*E*) Isomer: ^{13}C NMR (100 MHz, CDCl_3): δ = 21.16, 27.60, 28.30, 29.07, 32.35, 36.26, 38.21, 47.76, 91.46, 99.30, 125.71, 129.18, 135.73, 137.21, 140.59, 153.82 ppm. GC–MS: m/z (%) = 398 (9) $[\text{M}]^+$, 396 (8), 268 (21), 115 (37), 105 (42), 91 (43), 79 (35), 57 (100), 41 (86). $\text{C}_{20}\text{H}_{28}\text{Te}$ (396.02): calcd. C 60.65, H 7.13; found C 60.65, H 6.87.

S-(Diphenylphosphinoyl)methyl Ethanethioate (13): Thioacetic S-acid (761 mg, 10 mmol) in THF (40 mL) was added drop wise to a solution of NaH (dry 95%; 328 mg, 13 mmol) in THF (20 mL) at 0 °C. The reaction was stirred at room temp. for 30 min, and a solution of tosylate **2** (3.86 g, 10 mmol) in THF (40 mL) was slowly added at 0 °C. The reaction was stirred at room temp. for 30 min and water was added, and the mixture was extracted with ethyl acetate. The organic layer was washed with water, dried (MgSO_4), and filtered, and the solvent was removed under reduced pressure. The residue was purified by column chromatography (hexanes/ethyl acetate, 6:4). Yield 76%. ^1H NMR (200 MHz, CDCl_3): δ = 2.24 (s, 3 H), 3.78 (d, J_{PH} = 8.387 Hz, 2 H), 7.46–7.54 (m, 6 H), 7.73–7.82 (m, 4 H) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ = 26.93 (d, J_{PC} = 70.64 Hz), 29.71, 128.35 (d, J_{PC} = 12.01 Hz), 130.72 (d, J_{PC} = 9.18 Hz), 130.83 (d, J_{PC} = 103.14 Hz), 132.01 (d, J_{PC} = 2.83 Hz), 192.65 ppm. IR (KBr): $\tilde{\nu}$ = 1126, 1192, 1439, 1704 cm^{-1} .

Diethyl [(Diphenylphosphinoyl)methylthio]methylphosphonate (14): NaOH (3 M, 10 mL) was added to a solution of thiophosphane oxide (**13**; 2.90 g, 10 mmol) and methanol (10 mL). The mixture was stirred at room temp. for 30 min. The temperature was reduced to 0 °C, and iodomethyl phosphonate (2.78 g, 10 mmol) in CH_3CN (20 mL) was added. The reaction was stirred overnight at room temp., water was added, and the mixture was extracted with ethyl acetate. The organic layer was washed with ammonium chloride, dried (MgSO_4), and filtered, and the solvent was removed under vacuo. The residue was purified by recrystallization ($\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$, 1:9). Yield: 72%. M.p. 96–98 °C. ^1H NMR (200 MHz, CDCl_3): δ = 1.30 (t, J = 7.1 Hz, 6 H), 2.94 (d, J_{PH} = 12.0 Hz, 2 H), 3.62 (d, J_{PH} = 7.0 Hz, 2 H), 4.13 (qui, J = 7.3 Hz, 4 H), 7.27–7.55 (m, 6 H), 7.74–7.84 (m, 4 H) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ = 16.32 (d, J_{PC} = 6.13 Hz), 25.32 (d, J_{PC} = 148.6 Hz), 29.62 (d, J_{PC} = 70.54 Hz), 62.63 (d, J_{PC} = 6.90 Hz), 128.56 (d, J_{PC} = 11.5 Hz), 131.04 (d, J_{PC} = 9.97 Hz), 131.82 (d, J_{PC} = 100.45 Hz), 132.02 (d,

$J_{PC} = 2.30$ Hz) ppm. IR (KBr): $\tilde{\nu} = 959, 1021, 1177, 1245, 1484$ cm⁻¹. GC-MS: m/z (%) = 398 (6) [M]⁺, 247 (12), 217 (14), 216 (41), 215 (100), 201 (13), 141 (14), 125 (14), 77 (19), 47 (21).

Acknowledgments

The authors thank FAPERGS, CAPES, and MCT/CNPq for financial support.

- [1] a) J. V. Comasseto, L. W. Ling, N. Petragnani, H. A. Stefani, *Synthesis* **1997**, 373–403; b) J. V. Comasseto, R. E. Barrientos-Astigarraga, *Aldrichimica Acta* **2000**, 33, 66–78; c) M. L. Vieira, F. K. Zinn, J. V. Comasseto, *J. Braz. Chem. Soc.* **2001**, 12, 586–596; d) D. S. Lüdtkke, R. B. Panatieri, A. L. Braga, G. Zeni, *Chem. Rev.* **2006**, 106, 1032–1076; e) V. K. Aggarwal, C. L. Winn, *Acc. Chem. Res.* **2004**, 37, 611–620; f) Y. Tang, S. Ye, X. L. Sun, *Synlett* **2005**, 2720–2730.
- [2] a) N. Petragnani, *Tellurium in Organic Synthesis (Best Synthetic Methods)*, Academic Press, London, UK, **1994**; b) N. Petragnani in *Organotellurium Compounds in Organic Synthesis* (Ed.: A. Mc Killop), Pergamon Press, New York, **1994**, vol. 11, ch. 14; c) G. H. Whitham, *Oxford Chemistry Primers Number 33: Organosulfur Chemistry* (Ed.: S. G. Davies), Oxford University Press, Oxford, **1995**.
- [3] N. K. Gusarova, A. A. Tatarinova, L. M. Sinogovskaya, *Sulfur Rep.* **1991**, 11, 1–50.
- [4] C. C. Silveira, G. Perin, R. G. Jacob, A. L. Braga, *Phosphorus Sulfur Silicon Relat. Elem.* **2001**, 172, 55–100.
- [5] a) C. C. Silveira, P. Boeck, A. L. Braga, *Tetrahedron Lett.* **2000**, 41, 1867–1869; b) C. C. Silveira, G. Perin, P. Boeck, A. L. Braga, N. Petragnani, *J. Organomet. Chem.* **1999**, 584, 44–47; c) C. C. Silveira, G. Perin, A. L. Braga, M. J. Dabdoub, R. G. Jacob, *Tetrahedron* **1999**, 55, 7421–7432; d) C. C. Silveira, P. C. S. Santos, A. L. Braga, *Tetrahedron Lett.* **2002**, 43, 7517–7520; e) C. C. Silveira, M. L. Begnini, P. Boeck, A. L. Braga, *Synthesis* **1997**, 221–228; f) C. C. Silveira, G. Perin, A. L. Braga, N. Petragnani, *Synlett* **1995**, 58–60; g) C. C. Silveira, R. C. Guadagnin, A. L. Braga, *Tetrahedron Lett.* **2003**, 44, 5703–5705.
- [6] a) C. W. Lee, Y. J. Koh, D. Y. Oh, *J. Chem. Soc. Perkin Trans. 1* **1994**, 717–719; b) L. Testaferri, M. Tiecco, M. Tingoli, D. Chianelli, *Tetrahedron* **1986**, 42, 63–69; c) J. V. Comasseto, N. Petragnani, *J. Organomet. Chem.* **1978**, 152, 295–304.
- [7] a) H. Okamura, M. Miura, K. Kosugi, H. Takei, *Tetrahedron Lett.* **1980**, 21, 87–90; b) M. Tingoli, M. Tiecco, L. Testaferri, A. Temperini, G. Pelizzi, A. Bacci, *Tetrahedron* **1995**, 51, 4691–4700; c) J. Gerard, L. Hevesi, *Tetrahedron* **2001**, 57, 9109–9121.
- [8] M. Tingoli, M. Tiecco, L. Testaferri, D. Chianelli, *Gazz. Chim. Ital.* **1991**, 121, 59–61.
- [9] L. Hevesi, B. Hermans, C. Allard, *Tetrahedron Lett.* **1994**, 36, 6729–6730.
- [10] Y. Nishibayashi, C. S. Cho, K. Ohe, S. Uemura, *J. Organomet. Chem.* **1996**, 526, 335–339.
- [11] a) A. L. Braga, D. S. Lüdtkke, F. Vargas, R. K. Donato, C. C. Silveira, H. A. Stefani, G. Zeni, *Tetrahedron Lett.* **2003**, 44, 1779–1781; b) A. L. Braga, F. Vargas, G. Zeni, C. C. Silveira, L. H. de Andrade, *Tetrahedron Lett.* **2002**, 43, 4399–4402; c) A. L. Braga, L. H. Andrade, C. C. Silveira, A. V. Moro, G. Zeni, *Tetrahedron Lett.* **2001**, 42, 8563–8565; d) G. Zeni, P. H. Menezes, A. V. Moro, A. L. Braga, C. C. Silveira, H. A. Stefani, *Synlett* **2001**, 1473–1475; e) Y. Nishibayashi, C. S. Cho, S. Uemura, *J. Organomet. Chem.* **1996**, 507, 197–200; f) G. Zeni, J. V. Comasseto, *Tetrahedron Lett.* **1999**, 40, 2117–2118; g) S. K. Kang, S. W. Lee, M. S. Kim, H. S. Kwon, *Synth. Commun.* **2001**, 31, 1721–1725.
- [12] a) C. C. Silveira, A. L. Braga, A. S. Vieira, G. Zeni, *J. Org. Chem.* **2003**, 68, 662–665; b) C. Raminelli, J. Gargalaka Jr, C. C. Silveira, J. V. Comasseto, *Tetrahedron Lett.* **2004**, 45, 4927–4930.
- [13] S. Uemura, K. Ohe, J. R. Kim, K. Kudo, N. Sugita, *J. Chem. Soc. Chem. Commun.* **1985**, 271–272.
- [14] a) K. Ohe, H. Takahashi, S. Uemura, N. Sugita, *J. Organomet. Chem.* **1987**, 326, 35–47; b) K. Ohe, H. Taka-hashii, S. Uemura, N. Sugita, *J. Org. Chem.* **1987**, 52, 4859–4863.
- [15] a) Y. Z. Huang, X. S. Mo, *Synlett* **1998**, 93–95; b) X. S. Mo, Y. Z. Huang, *Tetrahedron Lett.* **1995**, 36, 3539–3542; c) M. J. Dabdoub, M. L. Begnini, T. M. Cassol, P. G. Guerrero Jr, C. C. Silveira, *Tetrahedron Lett.* **1995**, 36, 7623–7626; d) A. Ogawa, Y. Tsuboi, R. Obayashi, K. Yokoyama, I. Ryu, N. Sonoda, *J. Org. Chem.* **1994**, 59, 1600–1601; e) M. J. Dabdoub, R. G. Jacob, J. T. B. Ferreira, V. B. Dabdoub, F. A. Marques, *Tetrahedron Lett.* **1999**, 40, 7159–7162.
- [16] Y. Z. Huang, X. S. Mo, *Tetrahedron Lett.* **1998**, 39, 1945–1948.
- [17] J. Terao, N. Kambe, N. Sonoda, *Tetrahedron Lett.* **1996**, 37, 4741–4744.
- [18] R. E. Barrientos-Astigarraga, D. N. Moraes, J. V. Comasseto, *Tetrahedron Lett.* **1999**, 40, 265–268.
- [19] T. Kanda, T. Sugiro, N. Kambe, N. Sonoda, *Phosphorus Sulfur Silicon Relat. Elem.* **1992**, 67, 103–106.
- [20] W. B. Jang, D. Y. Oh, C. W. Lee, *Tetrahedron Lett.* **2000**, 41, 5103–5106.
- [21] a) F. C. Tucci, A. Chieffi, J. V. Comasseto, J. P. Marino, *J. Org. Chem.* **1996**, 61, 4975–4984; b) J. V. Comasseto, J. Berriel, *Synth. Commun.* **1990**, 20, 1681–1685; c) D. N. Moraes, R. E. Barrientos-Astigarraga, P. Castelani, J. V. Comasseto, *Tetrahedron* **2000**, 56, 3327–3337; d) M. A. Araujo, R. E. Barrientos-Astigarraga, R. M. Ellensohn, J. V. Comasseto, *Tetrahedron Lett.* **1999**, 40, 5115–5118.
- [22] J. P. Marino, F. C. Tucci, J. V. Comasseto, *Synlett* **1993**, 761–763.
- [23] M. A. Araujo, J. V. Comasseto, *Synlett* **1995**, 1145–1148.
- [24] X. Huang, C. Q. Zhao, *Synth. Commun.* **1997**, 27, 237–241.
- [25] a) A. Chieffi, J. V. Comasseto, *Tetrahedron Lett.* **1995**, 35, 4063–4066; b) A. Chieffi, J. V. Comasseto, *Synlett* **1995**, 671–674; c) Y. Z. Huang, X. S. Mo, L. Wang, *Tetrahedron Lett.* **1998**, 39, 419–422.
- [26] M. J. Dabdoub, V. B. Dabdoub, J. P. Marino, *Tetrahedron Lett.* **2000**, 41, 437–440; M. J. Dabdoub, V. B. Dabdoub, J. P. Marino, *Tetrahedron Lett.* **2000**, 41, 433–436.
- [27] S. M. Barros, J. V. Comasseto, M. J. Dabdoub, V. Dabdoub, *Organometallics* **1989**, 8, 1661–1665.
- [28] H. Hellmann, J. Bader, *Tetrahedron Lett.* **1961**, 2, 724–729.
- [29] S. E. Tkachenko, A. N. Yarkovich, S. V. Timofeev, E. N. Tsvetkov, *J. Gen. Chem. USSR (Engl. Transl.)* **1988**, 58, 531–536.
- [30] a) Z. Rohlik, P. Holzhauser, J. Kotek, J. Rudovsky, I. Nemec, P. Hermann, I. Lukes, *J. Organomet. Chem.* **2006**, 691, 2409–2423; b) G. M. Oliveira, *Quím. Nova* **2001**, 24, 133–134.
- [31] J. H. van Steenis, A. van der Gen, *Eur. J. Org. Chem.* **2001**, 897–910.
- [32] W. Wegener, *Z. Chem.* **1971**, 11, 262–262.
- [33] J. Clayden, S. Warren, *Angew. Chem. Int. Ed. Engl.* **1996**, 35, 241–270.
- [34] J. I. Grayson, S. Warren, *J. Chem. Soc. Perkin Trans. 1* **1977**, 2263–2272.
- [35] B. L. Nilsson, L. L. Kiessling, R. T. Raines, *Org. Lett.* **2001**, 3, 9–12.
- [36] D. P. Thompson, P. Boudjouk, *J. Org. Chem.* **1988**, 53, 2109–2112.

Received: May 2, 2007
 Published Online: August 3, 2007