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Non-catalyzed addition of secondary phosphine chalcogenides to divinyl chalcogenides under solvent-free conditions

Nina K. Gusarova^a, Nataliya A. Chernysheva^a, Svetlana V. Yas'ko^b, Lyudmila V. Klyba^a and Boris A. Trofimov^a

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ABSTRACT

Secondary phosphine chalcogenides, R₂PX (R=(CH₂)₂Ph, Ph; X = S, Se), react with divinyl chalcogenides, (CH₂=CH)₂Y (Y = S, Se, Te), at the 2:1 molar ratio (80–82°C, 56–80 h) in the absence of both catalysts (initiators) and solvents to quantitatively afford the corresponding anti-Markovnikov diadducts. Even at the equimolar reactant ratio, the diadducts are the major products, though monoadducts are also formed. When Y = Te, vinylphosphine chalcogenides and metal Te are obtained, thus showing that divinyl telluride behaves as the vinylating agent.



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Secondary phosphine chalcogenides; divinyl chalcogenides; catalyst- and solvent-free addition; synthesis; α ; ω -diphosphine chalcogenides

1. Introduction

Tertiary α, ω -diphosphines and α, ω -diphosphine chalcogenides continue to attract significant attention of researchers. Currently, these important organophosphorus compounds find widespread application as prospective ligands for the design of metal complex catalysts,[1–11] precursors of pharmaceutical compounds,[12–19] as well as special solvents-stabilizers for the preparation of nano-sized semi-conducting materials.[20–28] α, ω -Diphosphine chalcogenides bearing chalcogenoalkane moieties are of special interest as polydentate hemilabile ligands.[29–40]

Among the most straightforward approaches to the synthesis of functional α , ω -diphosphines and phosphine chalcogenides is the reaction of secondary phosphines and

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phosphine chalcogenides with available divinyl chalcogenides, easily prepared from acetylene and elemental sulfur, selenium and tellurium in the presence of superstrong bases of the type KOH – polar non-hydroxylic solvent (DMSO, HMPA).[41–43]

Earlier it has been reported that diaddition of secondary phosphine and phosphine chalcogenides to divinyl chalcogenides (divinyl sulfide,[9] divinyl selenide,[44] divinyl telluride,[45,46] divinyl sulfoxide,[47] divinyl sulfone,[48,49] as well as divinyl ethers of glycols [50]) proceeds in the presence of radical initiators [9,44–46] or bases [47–49,51,52] and, as a rule, in organic solvents.

In recent years, catalyst- and solvent-free reactions attract a particular attention. This is especially important in view of modern requirements of green chemistry. For example, it has been shown that secondary phosphine and phosphine chalcogenides react with diverse monoalkenes (including functionalized ones) under non-catalyst and non-solvent conditions to afford anti-Markovnikov adducts.[53–57]

2. Results and discussion

To extend the preparative scope of the novel environmentally benign method for the synthesis of functional phosphine chalcogenides and to gain additional knowledge about the C–P bond formation from PH-addends and alkenes under non-catalytic solvent-free conditions, in the present work, we have studied the reaction of secondary phosphine sulfides and phosphine selenides with available [41–43] divinyl chalcogenides.

The experiments have shown that bis(2-phenethyl)phosphine sulfide 1, bis(2-phenethyl)phosphine selenide 2 and diphenylphosphine sulfide 3 react with divinyl sulfide 4 and divinyl selenide 5 (molar ratio of the starting reagents is 2:1) upon heating ($80-82^{\circ}C$, 56-80 h) in the absence of catalysts and solvents to afford the corresponding diadducts **6a-6d** in almost quantitative yields (Table 1, Entries 1–4). It should be emphasized that the radical scavengers (hydroquinone or TEMPO) do not inhibit the addition of phosphine chalcogenide 1 to divinyl sulfide 4 (Table 1, Entries 5, 6). Moreover, in the dark, this reaction proceeds with the same efficiency as in the light (Table 1, Entry 7).

Using bis(2-phenethyl)phosphine oxide as an example, it has been found that secondary phosphine oxides do not react with divinyl chalcogenides **4** and **5** under the conditions elaborated.

The attempts to direct this reaction at the preferable formation of the monoadduct by heating (at 43–45°; 50–53° or 80–82°C) phosphine sulfides **1**, **3** with divinyl sulfide **4** or divinyl selenide **5** (their molar ratio 1:1) do not give the desired result. In all the experiments, mixtures of mono – **7a,b,d** and diadducts **6a,b,d** are formed, the latter being significantly (\sim threefold times) prevailing. This indicates a much higher addition rate of the phosphine chalcogenides to the monoadducts (Scheme 1).

Adducts **6d** and **7d** (obtained from divinyl selenide and phosphine sulfide **3**) are easily isolated from the reaction mixture in 22% and 57% yields, respectively. At the same time, separation of mono- and diadducts **7a**,**7b** and **6a**,**6b** on a chromatographic column has met with no success, since they have almost the same solubility in most organic solvents (benzene, ether, chloroform, acetone and ethanol) and close $R_{\rm f}$ values.

The reaction mechanism is of a special interest. As far as the addition takes place with equal efficiency both in the light and in the dark and radical scavenges such as TEMPO and hydroquinone do not influence the process, one should decline the radical mechanism. As

a probable rationale of the mechanism, the electrophilic attack of the positively charged phosphorus atom of the phosphine chalcogenides at the β -carbon of vinyl chalcogenides may be admitted (Scheme 2). Such an attack should be facilitated by the negative charge

Table 1. Synthesis of α, ω -diphosphine chalcogenides **6a–6d** under catalyst- and solvent-free conditions^a.



R = (CH₂)₂Ph, Ph; X = S, Se; Y = S, Se



(continued).

Table 1. Continued.



^aStandard reaction condition: molar ratio phosphine chalcogenide/divinyl chalcogenide = 2:1, 80–82°C, argon. ^bExperiment was carried out in the presence of hydroquinone (10 wt%).

^cExperiment was carried out in the presence of TEMPO (5 wt%).

^dExperiment was carried out in dark.



R = $(CH_2)_2$ Ph, Y = S (4, 6a, 7a); R = $(CH_2)_2$ Ph, Y = Se (5, 6b, 7b); R = Ph, Y = Se (5, 6d, 7d)

Scheme 1. Synthesis of monoadducts 7a,b,d.



Scheme 2. A possible generation of intermediate A.

at this atom and stabilization of the emerging positive charge at the α -carbon atom by the lone electron pair of the chalcogen atom (intermediate A).

This process should be additionally favored by simultaneous hydrid transfer from the phosphorus atom to the carbenium center. Consequently, all this is likely realized in the four-membered transition state **B**. Of course, the six-membered transition state **C** with the participation of two molecules of the phosphine chalcogenides, having more favorable valence angles, should not be excluded.





Scheme 3. Reaction of divinyl telluride with secondary phosphine sulfides.

A higher rate of the addition to the mono-adducts (the advantageous formation of the diadducts, see above) also requires rationalization. In terms of Scheme 1, this phenomenon may be understood as an activation of the remaining double bond due to its additional polarization under the intramolecular through-space influence from the polarized phosphine chalcogenide moieties in the appropriate conformation \mathbf{D} of the mono-adduct.



It appears that the reaction of divinyl telluride with secondary phosphine sulfide under similar conditions takes another direction. So, upon heating (80–82°C, 125 h) of divinyl



Figure 1. Ion fragmentation m/z 732 (¹³⁰Te) of diadduct **8** in MS/MS TOF/TOF laser desorption/ionization spectrum.

telluride with phosphine sulfide 1, instead of the expected diadduct 8, vinylphosphine sulfide 9 is formed in 72% yield, metal tellurium being also isolated. This reaction likely occurs via the initial generation of diadduct 8, which further decomposes to give vinylphosphine sulfide 9 and metal tellurium (Scheme 3). Thus, in this case, divinyl telluride is a vinylating agent relative to secondary phosphine sulfides.

Diadduct **8** has been detected in the reaction mixture by using the MSMS technique (Figure 1).

3. Conclusion

In conclusion, a convenient, efficient and atom-economic method for the synthesis of functionalized diphosphine chalcogenides via the catalyst- and solvent-free reaction of secondary phosphine sulfides and phosphine selenides with divinyl sulfide and divinyl selenide has been elaborated. The products obtained represent polydentate multifaceted ligands, intermediates for drug design as well as for the generation of nano-sized semi-conductors.

4. Experimental

4.1. General

The C, H, S microanalyses were performed on a Flash EA 1112 CHNS-O/MAS analyzer, while the P and Se content were determined by combustion method. IR spectra were run on a Bruker Vertex 70 instrument. The ¹H, ¹³C, ³¹P and ⁷⁷Se NMR spectra were recorded on a Bruker DPX 400 and Bruker AV-400 spectrometer (400.13, 100.61, 161.98 and 76.31 MHz, respectively). 85% H₃PO₄/H₂O was employed as external standard for ³¹P NMR; hexamethyldisiloxane was used for ¹H, ¹³C NMR and Me₂Se was the external standard for ⁷⁷Se NMR. Melting points (uncorrected) were measured on a Kofler micro hot-stage apparatus. Laser desorption ionization MS/MS TOF/TOF mass spectrum was recorded on UltraFlex III TOF/TOF (Bruker Daltonics GmbH, Germany), equipped with a pulse nitrogen laser (337 nm) using FlexControl (Bruker Daltonics, Germany) software (version 3.3) in a reflectron modi. The spectra were processed using FlexAnalysis 3.3 software (Bruker Daltonics, Germany). Positively charged ions were fixed. Metastable ion peaks (PSD), decomposed in field-free space, were determined in LIFT mode. Mass spectra were calibrated using Proteo Mass set (Sigma, Germany). Samples were prepared by the Dried-Drop Method: 0.5 µL of the sample (2.3 pMol) solution in CHCl₃ (Merk, Germany) was deposited onto the target NALDITM (Nanosys, Inc. Palo Alto, CA, USA), having a nano-structured surface allowing to study the analyte without matrix, and allowed to air-dry (for several minutes) at room temperature.

All steps of the experiment were carried out in argon atmosphere. Divinyl chalcogenides were readily prepared according to the published procedure.[41–43] Secondary phosphine chalcogenides 1, 2 were synthesized by oxidation of the corresponding phosphines with powdered sulfur or selenium. The initial phosphine was prepared from red phosphorus and styrene as described in the literature.[58] Diphenylphosphine sulfide 3 was prepared by oxidation of commercially available diphenylphosphine (Aldrich) with elemental sulfur.

4.2. General procedure for synthesis of $\alpha_{,\omega}$ -diphosphine chalcogenides 6a–6d

A mixture of secondary phosphine chalcogenide 1–3 and divinyl chalcogenide 4, 5 (molar ratio 2:1) was stirred at 80–82°C for 56–80 h under argon atmosphere. The reaction was monitored by ³¹P NMR following the disappearance of the signal of the starting phosphine chalcogenide ($\delta_P = 3 \div 23$ ppm) and simultaneous appearance of a new signal at 38 ÷ 49 ppm, corresponding to tertiary phosphine chalcogenide **6a**–6**d**. After the reaction completion, the crude product was dissolved in a small amount of chloroform and reprecipitated to hexane to give compounds **6a**–d in 95–98% yields.

4.2.1. 2-[2-(Diphenethylphosphorothioyl)ethyl]sulfanylethyl(diphenethyl)phosphine sulfide (6a)

Colorless oil; yield: 0.38 g (95%). ¹H NMR (400.13 MHz, CDCl₃): $\delta = 2.13$ [m, 12 H, $CH_2P(CH_2)_2$], 2.81 (m, 4 H, CH_2S), 2.93 (m, 8 H, $PhCH_2$), 7.18–7.31 (m, 20 H, Ph). ¹³C NMR (100.61 MHz, CDCl₃): $\delta = 24.97$ (d, ² $J_{PC} = 2.0$ Hz, SCH₂), 28.59 (d, ² $J_{PC} = 3.1$ Hz, PhCH₂), 31.04 (d, ¹ $J_{PC} = 45.5$ Hz, PCH₂CH₂S), 33.29 (d, ¹ $J_{PC} = 48.2$ Hz, PCH₂CH₂Ph), 126.65 (C_p, Ph), 128.24, 128.76 (C_{o,m}, Ph), 140.33 (d, ³ $J_{PC} = 14.2$ Hz, C_i, Ph). ³¹P NMR (161.98 MHz, CDCl₃): $\delta = 48.8$. IR (neat, cm⁻¹): 3084, 3061, 3026, 3001 (ν =CH of phenyl rings), 2922, 2904, 2861 (ν CH), 1952, 1878, 1809, 1753, 1602, 1584, 1496 (ν C=C of phenyl rings), 1452, 1404 (δ CH₂), 1274, 1214, 1137, 1072, 1027, 1008, 951, 911, 836 (δ CH of phenyl rings), 752 br.c (ν P–C), 699 (δ CH of phenyl rings), 598 (ν P=S). Anal. Calcd for C₃₆H₄₄P₂S₃: C, 68.11; H, 6.99; P, 9.76; S, 15.15. Found: C, 68.19%; H, 7.23%; P, 9.67%; S, 14.85%.

4.2.2. 2-[2-(Diphenethylphosphorothioyl)ethyl]selanylethyl(diphenethyl)phosphine sulfide (**6b**)

Colorless oil; yield: 0.54 g (98%). ¹H NMR (400.13 MHz, CDCl₃): $\delta = 2.17$ (m, 12 H, CH_2PCH_2), 2.82 (m, 4 H, CH_2Se), 2.94 (m, 8 H, $PhCH_2$), 7.18–7.25 (m, 20 H, Ph). ¹³C NMR (100.61 MHz, CDCl₃): $\delta = 15.20$ (d, ² $J_{PC} = 3.7$ Hz, CH_2Se), 28.53 (PhC H_2), 32.08 (d, ¹ $J_{PC} = 44.2$ Hz, PCH_2CH_2Se), 32.93 (d, ¹ $J_{PC} = 47.5$ Hz, $PhCH_2CH_2P$), 126.61 (C_p , Ph), 128.23, 128.71 ($C_{o,m}$, Ph), 140.30 (d, ³ $J_{PC} = 13.4$ Hz, C_i , Ph). ³¹P NMR (161.98 MHz, CDCl₃): $\delta = 49.5$. ⁷⁷Se NMR (76.31 MHz, CDCl₃): $\delta = 249$ (CH₂SeCH₂). IR (neat, cm⁻¹): 3084, 3061, 3026, 3001 (ν =CH of phenyl rings), 2925, 2854 (ν CH), 1602, 1583, 1496 (ν C=C of phenyl rings), 1453, 1405 (δ CH₂), 1254, 1214, 1179, 1121, 1081, 1047, 1029, 1006, 949, 910, sh 888, 873, sh 832, sh 808 (δ CH of phenyl rings), br.c 750 (ν P–C), 698 (δ CH of phenyl rings), sh 612, 596 (ν P=S). Anal. Calcd for C₃₆H₄₄P₂S₂Se: C, 63.40; H, 6.51; P, 9.11; S, 9.39; Se, 11.61. Found: C, 63.46%; H, 6.59%; P, 8.96%; S, 9.48%; Se, 11.51%.

Physical-chemical and spectral data (NMR ¹H, ³¹P) were identical to those for the compound obtained previously from phosphine sulfide **1** and divinyl selenide under radical initiation (75°C, AIBN, 1,4-dioxane).[44]

4.2.3. 2-[2-(Diphenethylphosphoroselenoyl)ethyl]selanylethyl(diphenethyl) phosphine selenide (6c)

Light yellow oil; yield: 0.55 g (95%). ¹H NMR (400.13 MHz, CDCl₃): $\delta = 2.28$ (m, 12 H, CH₂PCH₂), 2.83 (m, 8 H, PhCH₂), 2.94 (m, 4 H, CH₂Se), 7.19–7.25 (m, 20 H, Ph). ¹³C NMR (100.61 MHz, CDCl₃): $\delta = 15.72$ (d, ²*J*_{PC} = 2.7 Hz, CH₂Se), 29.04 (PhCH₂), 31.35

(d, ${}^{1}J_{PC}$ = 36.5 Hz, PCH₂CH₂Se), 32.23 (d, ${}^{1}J_{PC}$ = 40.4 Hz, PhCH₂CH₂P), 126.36 (C_p, Ph), 127.99, 128.44 (C_{o,m}, Ph), 139.80 (d, ${}^{3}J_{PC}$ = 13.6 Hz, C_i, Ph).³¹P NMR (161.98 MHz, CDCl₃): δ = 38.9. ⁷⁷Se NMR (76.31 MHz, CDCl₃): δ = -387 (d, ${}^{1}J_{P-Se}$ = 702.0 Hz, P = Se), 252 (CH₂SeCH₂). IR (neat, cm⁻¹): 3084, 3061, 3026, 3001 (ν =CH of phenyl rings), 2924, 2854 (ν CH), 1602, 1583, 1496 (ν C=C of phenyl rings), 1454, 1404 (δ CH₂), sh 1269, 1254, 1214, 1178, 1120, 1082, 1029, 1006, 949, 910, 888, 873 (δ CH of phenyl rings), br.c 753 (ν P-C), 698 (δ CH of phenyl rings), sh 572, 575 (ν P=Se). Anal. Calcd for C₃₆H₄₄P₂Se₃: C, 55.78; H, 5.70; P, 7.97; Se, 30.57. Found: C, 56.01%; H, 5.69%; P, 7.84%; Se, 30.46%.

Physical-chemical and spectral data (NMR ¹H, ³¹P) were identical to those for the compound obtained previously from phosphine sulfide **2** and divinyl selenide under radical initiation (75°C, AIBN, 1,4-dioxane).[44]

4.2.4. 2-[2-(Diphenylphosphorothioyl)ethyl]selanylethyl(diphenyl)phosphine sulfide (6d)

White powder, m.p. 146–148°C; yield: 0.49 g (96%) prepared from diphenylphosphine sulfide **3** (1.5 mmol, 0.412 g) and divinyl selenide **4** (0.75 mmol, 0.100 g). ¹H NMR (400.13 MHz, CDCl₃): $\delta = 2.76$ (m, 8 H, PCH₂CH₂Se), 7.45–7.86 (m, 20 H, Ph). ¹³C NMR (100.61 MHz, CDCl₃): $\delta = 14.60$ (d, ²*J*_{PC} = 3.0 Hz, CH₂Se), 33.91 (d, ¹*J*_{PC} = 49.8 Hz, CH₂P), 128.7 (d, ²*J*_{PC} = 12.2 Hz, C_o), 131.1 (d, ³*J*_{PC} = 10.3 Hz, C_m), 131.5 (d, ⁴*J*_{PC} = 3.0 Hz, C_p). ³¹P NMR (161.98 MHz, CDCl₃): $\delta = 42.5$. IR (KBr, cm⁻¹): 3053 (ν =CH); 2926, 2892 (ν CH), 1477 (ν C=C of phenyl rings), 1463, 1430 (δ CH₂), 1317, 1268, 1172, 1102, 1010, 920, 873, sh 776 (δ CH of phenyl rings), 751 (ν P–C); 737, 719, 698 (δ CH of phenyl rings), sh 619, 603 (ν P=S). Anal. Calcd for C₂₈H₂₈P₂S₂Se: C, 59.05; H, 4.96; P, 10.88; S, 11.26; Se, 13.86. Found: C, 59.42%; H, 4.99%; P, 10.98%; S, 10.77%; Se, 13.84%.

Physical-chemical and spectral data (NMR ¹H, ³¹P) were identical to those for the compound obtained previously from phosphine sulfide **3** and divinyl selenide under radical initiation (75°C, AIBN, 1,4-dioxane).[44]

4.3. Synthesis of monoadducts (7a,b,d)

A mixture of phosphine sulfide **1** (1.0 mmol) and divinyl chalcogenide **4**, **5** (1.0 mmol) was stirred at $80-82^{\circ}$ C for 40-70 h (argon) following the disappearance of the signal of the starting phosphine sulfide **1** (³¹P NMR) to give a mixture of mono-**7a**, **7b** and diadducts **6a**,**6b** in a ratio of 70% and 30%, respectively, (³¹P NMR data).

Separation of mono- and diadducts **6a**, **7a** and **6b**, **7b** on a chromatographic column has met with no success, since they have almost the same solubility in most organic solvents (benzene, ether, chloroform, acetone, and ethanol) and close $R_{\rm f}$ values.

4.3.1. The mixture of adducts (6a and 7a)

¹H NMR (400.13 MHz, CDCl₃): $\delta = 2.14$ (m, 18 H, $CH_2P(CH_2)_2$ in **6a** and **7a**), 2.83 (m, 6 H, CH_2S in **6a** and **7a**), 2.94 (m, 12 H, $PhCH_2$ in **6a** and **7a**), 5.15 (d, 1 H, ${}^{3}J_{\text{HH}} = 16.7$ Hz,=CH₂ in **7a**), 5.23 (d, 1 H, ${}^{3}J_{\text{HH}} = 10.1$ Hz,=CH₂ in **7a**), 6.25 (dd, 1 H,=CH in **7a**), 7.14–7.26 (m, 30 H, Ph in **6a** and **7a**). ${}^{31}P$ NMR (161.98 MHz, CDCl₃): $\delta = 48.5$ (**7a**), 48.8 (**6a**).

4.3.2. The mixture of adducts (6b and 7b)

¹H NMR (400.13 MHz, CDCl₃): $\delta = 2.18$ (m, 18 H, CH_2PCH_2 in **6b** and **7b**), 2.84 (m, 6 H, CH₂Se in **6b** and **7b**), 2.94 (m, 12 H, PhCH₂ in **6b** and **7b**), 5.54 (d, 1 H, ³J_{HH} = 16.9 Hz,=CH₂ in **7b**), 5.78 (d, 1 H, ³J_{HH} = 9.8 Hz,=CH₂, in **7b**), 6.62 (dd, 1 H,=CH in **7b**), 7.19–7.26 (m, 30 H, Ph in **6b** and **7b**). ³¹P NMR (161.98 MHz, CDCl₃): $\delta = 49.3$ (**7b**), 49.5 (**6a**).

4.3.3. Diphenyl[2-(vinylselanyl)ethyl]phosphine sulfide (7d)

A mixture, prepared from diphenylphosphine sulfide **3** (1.0 mmol, 0.218 g) and divinyl selenide **4** (1.0 mmol, 0.133 g), containing mono-7**d** and diadduct **6d** in a ratio of 70% and 30%, respectively (³¹P NMR data), was dissolved in cold ether. Upon storage, a white powder, diadduct **6d** (0.226 g, 57%), was precipitated from the mixture. The ether solution was decanted, concentrated under reduced pressure and passed through a thin (5 mm) layer of Al₂O₃. The solvent was evaporated and the residue was dried at 1 mm Hg to give viscous monoadduct **7d** as light-yellow oil (0.054 g, 22%). ¹H NMR (400.13 MHz, CDCl₃): $\delta = 2.87$ (m, 4 H, PCH₂CH₂Se), 5.46 (d, 1 H, ³J_{HH} = 16.7 Hz, =CH₂), 5.73 (d, 1 H, ³J_{HH} = 9.6 Hz, =CH₂), 6.64 (dd, 1 H, CH=), 7.53 (m, 6 H, Ph), 7.89 (m, 4 H, Ph). ¹³C NMR (100.61 MHz, CDCl₃): $\delta = 16.26$ (d, ²J_{PC} = 2.0 Hz, CH₂Se), 33.96 (d, ¹J_{PC} = 49.2 Hz, CH₂P), 118.12 (=CH₂), 125.40 (CH=), 128.6 (d, ²J_{PC} = 74.4 Hz, C_i). ³¹P NMR (161.98 MHz, CDCl₃): $\delta = 41.9$. Anal. Calcd for C₁₆H₁₇PSSe: C, 54.70; H, 4.88; P, 8.82; S, 9.13; Se, 22.48. Found: C, 54.75%; H, 4.90%; P, 8.96%; S, 9.01%; Se, 22.38%.

Physical-chemical and spectral data (NMR ¹H, ³¹P) were identical to those for the compound obtained previously from phosphine sulfide **3** and divinyl selenide under radical initiation (75°C, AIBN, 1,4-dioxane).[44]

4.4. Reaction of phosphine sulfide 1 with divinyl telluride

A mixture of secondary phosphine sulfide 1 (1.5 mmol, 0.412 g) and divinyl telluride (0.75 mmol, 0.136 g) was stirred at 80–82°C for 125 h (argon) following the disappearance in the ³¹P NMR of the signal of the starting phosphine sulfide 1 at 21.3 ppm and simultaneous appearance of new signals at 51.3 ppm (the expected diadduct **8**) and 43.1 ppm (vinylphosphine sulfide **9**). As the reaction proceeded, the intensity of the signal corresponding to vinylphosphine sulfide **9** increased, while the intensity of the signal corresponding to diadduct **8** dropped. The presence of the expected diadduct **8** in the reaction mixture was proved by MSMS analysis: the spectrum showed a characteristic cluster of isotopic peaks of the molecular ion with m/z 732 (for ¹³⁰Te). After complete disappearance of the signal of the starting phosphine sulfide **1** in the ³¹P NMR spectrum, the reaction mixture contained diadduct **8** (51.3 ppm) and vinylphosphine sulfide **9** (43.1 ppm), the signal intensity being 5% and 95%, respectively. The crude product represents a viscous mass containing black inclusions (elemental tellurium). Ether (5 ml) was added to the product obtained, and the residue precipitated was separated and washed many times with ether to give 0.081 g of elemental tellurium.

The ether extracts were combined and evaporated under reduced pressure; the residue was dissolved in a small amount of ether and passed through thin layers of Al_2O_3 , and the ether was distilled to give 0.336 g (yield 72%) of vinylphosphine sulfide **9**.

4.4.1. Diphenethyl(vinyl)phosphine sulfide (9)

Light yellow viscous substance; yield: 0.336 g (72%). ¹H NMR (400.13 MHz, CDCl₃): $\delta = 2.16-2.28$ (m, 4 H, CH_2PCH_2), 2.84–3.05 (m, 4 H, $PhCH_2$), 6.21–6.57 (m, 3 H, CH=CH₂), 7.19–7.32 (m, 10 H, Ph). ³¹P NMR (161.98 MHz, CDCl₃): $\delta = 43.1$. Anal. Calcd for C₁₈H₂₁PS: C, 71.82; H, 6.99; P, 10.91; S, 10.51. Found: C, 71.93%; H, 7.03%; P, 10.47%; S, 10.57%.

Physical-chemical and spectral data were identical to the literature ones.[59]

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