Journal of Organometallic Chemistry 745-746 (2013) 126-132

Contents lists available at ScienceDirect

Journal of Organometallic Chemistry

journal homepage: www.elsevier.com/locate/jorganchem

Mass spectrometry and quantum chemical studies of the reaction of divinyl telluride with secondary phosphine sulfides: Synthesis of adducts

Nina K. Gusarova, Nataliya A. Chernysheva, Lyudmila V. Klyba, Vladimir A. Shagun, Svetlana V. Yas'ko, Vladimir I. Smirnov, Boris A. Trofimov*

A.E. Favorsky Irkutsk Institute of Chemistry, Siberian Branch of the Russian Academy of Sciences, 1 Favorsky Str., 664033 Irkutsk, Russian Federation

ARTICLE INFO

Article history: Received 24 April 2013 Received in revised form 16 July 2013 Accepted 18 July 2013

Keywords: Divinyl telluride Diphenylphosphine sulfide Adducts Mass spectra Quantum chemical calculations

ABSTRACT

Mass spectrometry and quantum chemical studies of the reaction of divinyl telluride with diphenylphosphine sulfide have been carried out. Reaction proceeds under radical initiation (AIBN, 63–68 °C, 2.5 h, THF, reactants molar ratio = 1:1) to afford the anti-Markovnikov monoadduct **1** and diadduct **2** in 67 and 23% yield, respectively. The former easily decomposes to give vinyldiphenylphosphine sulfide **3** (in 63% yield), ethylene and elemental tellurium, the structure of which represents mainly nano-sized powder consisting of agglomerates with average size of 350–450 nm. The comparative analysis of electron ionization mass spectra of compounds **1**, **2** and **3** indicates that the presence of tellurium atom in adducts **1** and **2** reduces stability of their molecular ions and hinders the elimination of sulfur atom. Under conditions of chemical ionization of phosphine sulfides **1** and **3**, the process of their protonation with CH⁵₅ followed by the elimination of sulfur atom from [HM]⁺ ion is dominant. These data are also confirmed by the results of quantum chemical calculations of the most stable protonated structures of phosphine sulfides **1** and **3**.

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

Divinyl telluride, which has become available due to the development of the method for its synthesis by direct reaction of acetylene with metal tellurium [1,2], represents a promising building block for organic and elementoorganic synthesis [2–6]. Divinyl telluride is capable of participating in different types of reactions due to the presence of several reactive sites in its molecule. For example, divinyl telluride reacts with bromine [5] and selenium dichloride [4] to afford the corresponding divinyl telluride bromide and -dichloride [4,5]. Divinyl telluride is oxidized by hydrogen peroxide to divinyl tellurone [2]. The reaction of divinyl telluride with organyl halogenides furnishes telluronium salts [2]. Under radical initiation [2], divinyl telluride adds thiols to the double bonds against the Markovnikov's rule to give mono- or diadducts [2].

Recently, we have shown that secondary phosphine sulfides under certain conditions (AIBN, 63-68 °C, reactants molar ratio

E-mail address: boris_trofimov@irioch.irk.ru (B.A. Trofimov).

2.1:1) react with divinyl telluride to deliver diadducts of anti-Markovnikov type in good yields [3].

The present communication reports essentially new data obtained by more detailed investigation of this reaction. The work is also aimed at mass spectrometry study of mono- and diadducts formed from divinyl telluride and secondary phosphine sulfides, since the data related to mass spectra of functional tertiary phosphine sulfides are limited in literature, and those of tertiary phosphine sulfides containing organyltelluride groups are absent at all. Quantum chemical calculations of the most stable protonated structures of these compounds have been performed to additionally explain the mechanism of phosphine sulfides decomposition.

2. Results and discussion

We have found that the heating (63–68 °C, 2.5 h, THF) of divinyl telluride with diphenylphosphine sulfide (their molar ratio is \sim 1:1) in the presence of AIBN regioselectively gives a mixture of mono- and diadducts **1** and **2** in 2.3:1 ratio (¹H and ³¹P NMR) (Scheme 1).

Diadduct **2** was isolated from the reaction mixture in 23% isolated yield. For this, the reaction mixture (after THF distillation) was diluted with ether and telluride **2** (insoluble in ether) was filtered.





CrossMark

^{*} Corresponding author. Fax: +7 3952 419346.

⁰⁰²²⁻³²⁸X/\$ – see front matter @ 2013 Elsevier B.V. All rights reserved. http://dx.doi.org/10.1016/j.jorganchem.2013.07.050



Scheme 1. The reaction of divinyl telluride with diphenylphosphine sulfide.

Monoadduct **1** (67% yield) remained in ether solution. It turned out that unlike diadduct **2**, which was stable on long storage under usual conditions, monoadduct **1** easily decomposed at room temperature to afford diphenylvinylphosphine sulfide **3** (63% yield) and metal tellurium. Besides, ethylene was also released (it was identified by qualitative reaction with potassium permanganate) (Scheme 2).

It should be noted that the morphology of metal tellurium, released during the decomposition of monoadduct **1** (Scheme 2), significantly differs from that of usual brand tellurium. For example, according to scanning electron microscopy (SEM), the synthesized metal tellurium represents mainly nano-sized powder consisting of agglomerates with average size of 350–450 nm (Fig. 1a), whereas brand tellurium comprises microcrystals of irregular form having rather big sizes (4–36 μ m) (Fig. 1b).

The structure of tertiary phosphine sulfides **1–3** synthesized has been confirmed by the data NMR and MS spectroscopy. One should emphasize that GS–MS study of these compounds may be of special interest since the results obtained are nontrivial and can essentially complement the known data related to behavior of tertiary phosphine sulfides in the conditions of electron and chemical ionization.

The analysis of electron ionization (EI) and chemical ionization positive ion (CI) mass spectra of functional tellurium-containing phosphine sulfides **1**, **2** has been carried out in comparison with the data of similar spectra of vinyldiphenylphosphine sulfide **3** and its heteroanalogue, vinyldiphenylphosphine oxide **4**.



The EI mass spectrum of phosphine sulfide **1** shows a characteristic cluster of isotopic peaks of molecular ion with m/z 402 (for ¹³⁰Te), the intensity of which is 5% from total ionic current.

The competition between the processes related to charge localization on phosphorus-containing or tellurium-containing



Scheme 2. Decomposition of diphenyl[2-(vinyltellanyl)ethyl]phosphine sulfide 1.

ions is won by the former, i.e. the most part of ionic current belongs to phosphorus-containing ions.

Decomposition of molecular ion of phosphine sulfide **1** proceeds via three competitive directions involving the cleavage of C–P and C–Te bonds and formation of $[M - C_2H_3]^+$ with m/z 375, $[M - C_2H_3Te]^+$ with m/z 245 and $[Ph_2PS]^+$ with m/z 217 (Scheme 3).

The most intensive peak is attributed to $[Ph_2PS]^+$ ion. Further decomposition of the formed ions obeys the known regularities established for phosphine sulfides bearing aromatic substituents [7].

It should be noted that during the fragmentation of compound **1**, sulfur atom remains intact both in molecular ion and main fragment ions. However, it is a common knowledge that phosphine sulfides are characterized by elimination of sulfur atom from M^+ [7–10]. Nevertheless, in the case of phosphine sulfide **1**, elimination of sulfur atom or sulfur-containing particles is observed only at deeper stages of the primary ions decomposition.

To estimate the effect of tellurium atom on character of molecular ion decomposition of adduct **1**, we have analyzed the fragmentation data obtained for diphenylvinylphosphine sulfide **3** and its oxygen analog **4**. Unlike tellurium-containing phosphine sulfide **1**, in the mass spectrum of phosphine sulfide **3**, the peak of molecular ion with m/z 244 possesses the highest intensity. Interestingly, the character of fragmentation of the latter coincides with decomposition of oxygen analog **4** [9]. Besides, the mass spectrum of phosphine sulfide **3** expectedly contains peaks of $[M - S]^+$ with m/z 212 (9%) and $[M - HS]^+$ with m/z 211(10%) ions, which are typical for nonfunctional triorganylphosphine sulfides [7–10], while in the mass spectrum of phosphine oxide **4**, peaks of $[M - O]^+$ and $[M - HO]^+$ ions are absent.

Thus, the comparative analysis of EI mass spectra of compounds 1 and 3 testifies that the presence of tellurium atom in monoadduct 1 reduces stability of its molecular ion and hinders the elimination of sulfur atom.

Unlike monoadduct **1**, under El diadduct **2** forms unstable molecular ion, the latter being decomposed at the moment of ionization. The mass spectrum of diadduct **2** contains peaks of three series of ions. The minor series of ions is generated via elimination of Ph₂PH molecule by the molecular ion to afford the ion with m/z434, which further decomposes to consecutively release radicals C₂H₃Te and HS or radical SPh (Scheme 4).

High intensity of the ion with m/z 244 (57%) is likely due to partial thermal decomposition of diadduct **2** in the input system.

Two main series of ions are owing to two odd-electron fragments with m/z 402 and m/z 218 formed by diadduct **2** molecular ion (Scheme 5). The fragment with m/z 402 contains Te atom, and character of its fragmentation (main ions with m/z 375, 245, 217, 183, 185, 139) completely corresponds to the decomposition of monoadduct **1** described above in detail (Scheme 3).

The fragmentation pattern of other ion with m/z 218 (main ions with m/z 185, 183, 152, 140, 109, 108, 107, 63) coincides with fragmentation of the initial diphenylphosphine sulfide (Scheme 6).

The study of Cl mass spectrum has shown that diphenyl[2-(vinyltellanyl)ethyl]phosphine sulfide **1** is easily protonated in a gas phase, and the cluster of peaks of the protonated molecular ion has the maximum intensity $[HM]^+$ ($I_{TIC} = 30\%$).

In the CI mass spectrum of monoadduct **1**, peaks of two series of ions are present. This indicates that ionization of tellurium-containing phosphine sulfide **1** proceeds via two different routes. A minor series of ions is caused by the C–P and C–Te bonds cleavage and is similar to those ions which are observed during EI (ions with m/z 245, m/z 217, Scheme 3). Generation of these ions can take place both at decomposition of the protonated molecular ion and as a result of ionization according to the mechanism of anion elimination (Scheme 7).



Fig. 1. SEM image of tellurium: a - prepared according to Scheme 2; b - brand one.



Scheme 3. The fragmentation pattern for the diphenyl[2-(vinyltellanyl)ethyl]phosphine sulfide **1** under electron ionization.

Second series of ions indicate the main direction of the decomposition and is associated with elimination of sulfur atom from $[HM]^+$ ion and the formation of the protonated molecular ion of diphenyl[2-(vinyltellanyl)ethyl]phosphine with m/z 371 (21%) (for ¹³⁰Te, Scheme 8).

In CI mass spectra of phosphine sulfide **3** and phosphine oxide **4** the peaks of the protonated molecular ions are predominant.

Decomposition of $[HM]^+$ ions for phosphine sulfide **3** is due to the elimination of sulfur atom (ion m/z 213) and benzene molecule (ion m/z 167, Scheme 9).

In CI mass spectrum of phosphine oxide 4 only one fragmental ion caused by elimination of a molecule of benzene (ion m/z 151, Scheme 10) is observed.

It should also be noted the CI ionization of all the compounds studied **1**, **3**, **4** involves the processes of electrophilic addition giving rise to $[M + C_2H_5]^+$ and $[M + C_3H_5]^+$ ions.

Thus, the protonation process usually prevails in the chemical ionization of compounds **1**, **3**, **4** with CH_5^+ . For decomposition of phosphine sulfide **1**, the elimination of sulfur atom from [HM]⁺ ion (Scheme 8) is typical, whereas during electron ionization, on the contrary, sulfur-containing ions make the major contribution to total ionic current (Scheme 3).

To study the chemical ionization-initiated decomposition of phosphine sulfides **1**, **3** and phosphine oxide **4** in the course of their interaction with CH_{5}^{\pm} cation, we have employed quantum chemical calculations of structural reorganization of different protonated forms of compounds **1**, **3** and **4**.

The calculations have been performed by (DFT) B3LYP method [11-13] using the SDD (compound 1) and 6-31G (d, p) (compounds) **3** and **4**) basis sets and GAUSSIAN 98 package program [14]. The most sterically preferable proton stabilization sites in phosphine sulfide 1 turn out to be unshared pairs of S and Te heteroatoms. Protonation of these sites under topologically favorable conditions proceeds almost without barrier and does not lead to isomeric reorganization of the compound. The structure **1**(**SH**⁺) protonated at thione center is thermodynamically most stable. The relative stability of **1**(**SH**⁺) structure is by 8.1 kcal/mol higher than that of 1(TeH⁺). The direct attack by a proton of phosphine sulfide 1 phosphorus atom is hindered to its spatial isolation. However, under chemical ionization, the protonation of phosphorus atom is quite probable. The calculation have shown that this process is associated with overcoming high activation barrier that leads to isomeric reorganization of the molecule. The reorganization is accompanied by the elimination of sulfur atom from a near-tosphere environment of the central atom and its subsequent stabilization due to the interaction with tellurium (Scheme 11).

The elimination of sulfur occurs via the transition state (**TS1**) (Fig. 2) with overcoming the barrier of 24.8 kcal/mol. Thermodynamic stability of $1(PH^+)$ structure (Fig. 2) is slightly lower than



Scheme 4. The minor pathway fragmentation for the molecular ion of diadduct 2 under EI.



Scheme 5. The major fragmentation pattern for the molecular ion of diadduct **2** under EI.

that of $1(\text{Te}H^+)$ form (2.0 kcal/mol). Optimum molecular structures of the initial compound **1**, its protonated forms $[1(SH^+), 1(TeH^+), 1(PH^+)]$ and transition state (**TS1**) are given in Fig. 2.

The most probable protonation sites in phosphine sulfide **3** and phosphine oxide **4** are S and O heteroatoms, respectively (molecular structures **3**(SH⁺) and **4**(OH⁺) are given in Fig. 3). Similar to phosphine sulfide **1**, protonation of phosphorus atom in compound **3** leads to the elimination of S heteroatom from near-to-sphere environment of the phosphorus atom. As a result, the protonated structure **3**(PH⁺) is stabilized in the state, where sulfur atom, coordinating with the vinyl fragment, forms the thiirane cycle (Scheme 12, Fig. 3). The activation barrier of this process is by 2.5 KKAJ/MOJE lower than that of **TS1** equaling 22.3 kcal/mol. Thermodynamic stability of **3**(**PH**⁺) is by 12.6 kcal/mol lower than that of **3**(**SH**⁺).

At the same time, the protonated structure of compound **4**, **4**(**PH**⁺) is not capable of initiating the formation of the oxirane cycle but leads to sigmatropic rearrangement of the vinyl fragment and generation of formation $P-O-CH=CH_2$ chain (Scheme 12, Fig. 3). The rearrangement barrier is 11.8 kcal/mol higher than the

similar barrier of compound **3** that is due to higher strength of the C=O bond as compared to the C=S bond. Thermodynamic stability of $4(PH^+)$ is by 16.5 kcal/mol higher than that of $4(OH^+)$ structure. Next in stability protonated structures of compounds **3** and **4** are formed via the interaction of proton with aromatic fragments of the compounds giving rise to bimolecular systems (A) and (B). The relative stability of these states are by 20.4 and 30.6 kcal/mol higher than those **3**(SH⁺) and **4**(OH⁺) structures.

Thus, the calculations have shown that the chemical ionization of monoadduct **1** most likely involves the elimination of vinyl-telluranyl fragment and sulfur atom, while chemical ionization of vinyldiphenylphosphine sulfide **3** leads to elimination of sulfur atom and the benzene molecule. Chemical ionization of vinyl-diphenylphosphine oxide **4** should result in the elimination of benzene molecule only. These conclusions are in good agreement with experimental data, the CI mass spectra of compounds **1**, **3** and **4**, (Schemes 7–10).

3. Conclusion

In conclusion, divinyl telluride reacts with diphenylphosphine sulfide in the presence of AIBN (reactants molar ratio = 1:1) to predominantly afford the anti-Markovnikov monoadduct 1 as well as diadduct **2**. The adduct **1** easily decomposes at room temperature to afford vinyldiphenylphosphine sulfide, i.e. divinyl telluride is vinylating agent of secondary phosphine sulfides. The data of electron ionization mass spectra of compounds **1**, **2** and **3** indicates that the presence of tellurium atom in adducts **1** and **2** reduces stability of their molecular ions and hinders the elimination of sulfur atom. At the same time, in chemical ionization with CH_5^+ followed by the elimination of sulfur atom from $[HM]^+$ ion is dominant. The results of quantum chemical calculations of the most stable protonated structures of phosphine sulfides **1** and **3** are discussed.



Scheme 6. The fragmentation pattern for the molecular ion of diphenylphosphine sulfide under EL



Scheme 7. Main fragment ions in the CI mass spectrum of diphenyl[2-(vinyltellanyl)ethyl]phosphine sulfide 1 formed according to the mechanism of anion elimination.



Scheme 8. The fragmentation pattern for the protonated molecular ion of adduct 1 under chemical ionization.

4. Experimental

4.1. General conditions

All steps of the experiment were carried out in argon atmosphere. Tetrahydrofuran was purified by distillation from sodium/ benzophenone ketyl.

4.2. Instruments

Fourier transform IR spectra were run on a Bruker Vertex 70 instrument. The ¹H and ³¹P NMR spectra were recorded on a Bruker AV-400 spectrometer (400.13 and 161.98 MHz, respectively) and referenced to H_3PO_4 (³¹P NMR) as external standard. Melting points (uncorrected) were measured on a Kofler micro hot stage apparatus. The microanalyses were performed on a Flash EA 1112 Series elemental analyzer. Microstructure and chemical composition of tellurium samples were studied using TM3000 scanning microscope (Hitachi) equipped with Quantax 50 analyzer.

El mass spectra were run on GC–MS QP-5050A Shimadzu mass spectrometer at 70 eV with the source temperature fixed at 200 °C. The compounds were introduced through a direct insertion probe heated at the minimum temperature necessary to obtain reproducible ion abundances. The chemical ionization mass spectra were obtained by using Agilent 5975C MSD instrument equipped with chemical ionization source. The source temperature was approximately 150 °C. Samples were introduced into the source by means of the gas chromatograph GC-6890N (Agilent Technologies) through capillary column HP-5MS (30 m \times 0.25 mm \times 0.25 μ m), the helium being the gas-carrier. Positive CI mass spectra were recorded with CH₄ as reagent gas.



Scheme 9. The fragmentation pattern for the protonated molecular ion 3 under chemical ionization.

4.3. Reagents

Starting divinyl telluride was prepared as described in the literature [1]. Diphenylphosphine sulfide was synthesized from equimolar amounts of diphenylphosphine and elemental sulfur in ethanol at room temperature.

4.4. The reaction of divinyl telluride with diphenylphosphine sulfide

A solution of divinyl telluride (0.078 g, 0.43 mmol) and AIBN (0.008 g, 5% from reactant weight) in THF (2 mL) was blown with argon and heated up to 60 °C on stirring with a magnetic stirrer. Then a solution of diphenylphosphine sulfide (0.09 g, 0.41 mmol) in THF (1 mL) was added drop-wise. The reaction mixture was stirred with a magnetic stirrer for 2.5 h at 63–68 °C. The solvent was removed under reduced pressure to give 0.13 g orange copper-like product. The latter, according to the ³¹P NMR data, consisted of monoadduct **1** (δ_p = 44.96 ppm) and diadduct **2** (δ_p = 45.00 ppm), the signals intensity being 70% and 30%, respectively. The ether

$$\begin{array}{cccc}
& & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & & \\ & & & \\ & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & &$$

Scheme 10. The fragmentation pattern for the protonated molecular ion ${\bf 4}$ under chemical ionization.



Scheme 11. Structural reorganization of phosphine sulfide **1** due to the protonation of phosphorus atom.



Fig. 2. Main structural characteristics of compound 1, its protonated forms and transition state (TS1) (B3LYP/SDD). The distances are given in angstroms.



Fig. 3. Molecular structures and main geometry characteristics of thermodynamically most stable protonated forms of compounds 3 and 4 (3LYP/6-31G(d,p). The distances are given in angstroms.





Scheme 12. Structural reorganization of phosphine sulfide 3 and phosphine oxide 4 due to the protonation of phosphorus atom.

(5 mL) was added to a mixture of mono- **1** and diadduct **2**. The residue precipitated. The ether was decanted and the procedure was repeated trice. The precipitate obtained was dried to afford 0.03 g (23%) of diadduct **2**. The ether extracts were combined, concentrated under reduced pressure and the residue was dried *in vacuo* to give orange viscous product A (0.085 g), containing black inclusions (elemental tellurium). According to ³¹P NMR spectrum (C₆D₆), product A is a mixture of monoadduct **1** (δ_p = 44.96 ppm) and diphenylvinylphosphine sulfide **3** (δ_p = 36.52 ppm). ¹H NMR (400.13 MHz, C₆D₆), δ 2.78–2.97 (m, 4H, CH₂ in **1**),

¹H NMR (400.13 MHz, C₆D₆), δ 2.78–2.97 (m, 4H, CH₂ in 1), 5.71–5.75 (d, 1H, ³J_{HH} = 17.6 Hz, =CH₂, in 1), 5.73–5.81 (m, 2H, = CH₂ in 3), 6.07–6.09 (d, 1H, ³J_{HH} 10.3 Hz, =CH₂, in 1), 6.47–6.55 (m, 1H, CH=in 3), 6.80–6.87 (dd, 1H, CH=in 1), 7.08 (m, 12H, *m*,p-H_{Ph} in 1 and 3), 7.79–7.84 (m, 8H, o-H_{Ph} in 1 and 3). MS analysis of ether solution of product A has shown that it represents a mixture of two compounds: diphenylvinylphosphine sulfide 3 with *m*/*z* 244 (mass spectrum is similar to the literature data [10]) and monoadduct 1 with *m*/*z* 402 (for ¹³⁰Te). In one day, the product A is transformed into product **B** containing only diphenylvinylphosphine sulfide 3 (GCMS) and metal tellurium. The ether (5 mL) was added to the product **B**, the residue precipitated was separated and washed many times with ether to give 0.022 g of elemental tellurium, which was analyzed by scanning electron microscopy.

The ether solution was evaporated *in vacuo* to furnish 0.046 g (63%) of diphenylvinylphosphine sulfide **3**. ¹H NMR (400.13 MHz, C₆D₆) δ 6.05–6.46 (m, 3H, CH=CH₂), 7.12 (m, 6H, Ph), 7.68 (m, 4H, Ph); ³¹P NMR (161.98 MHz, C₆D₆) δ 36.9; (spectral data were identical to the literature ones [10]).

4.5. 2-[2-(Diphenylphosphorothioyl)ethyl]tellanylethyl(diphenyl) phosphine sulfide (**2**)

Yield: 23%; white crystals; m.p: 146–150 °C (ether); ¹H NMR (400.13 MHz, C₆D₆): δ 2.80 (m 8H, CH₂), 7.07 (m 12H, *m*,*p*-H_{Ph}), 7.93 (m 8H, o-H_{Ph}). ³¹P NMR (161.98 MHz, C₆D₆): δ 44.99. IR (KBr, *v*, cm⁻¹): 3052 (=CH of phenyl rings), 2931, 2902 (CH), 1477 (C=C of phenyl rings), 1434, 1394 (δ CH₂), 1310, 1248, 1180, 1154, 1139, 1102, 1069, 1026, 998, 928, 841, 762 (δ CH of phenyl rings), sh 752 (P–C), 744, 715, 706, 699 (δ CH of phenyl rings), 675, 623, 611, 603 (P=S), 589 (C–Te), 499, 486, 456, 430. Anal. Calcd. for C₂₈H₂₈P₂S₂Te (618.2): C, 54.62; H, 4.47; P, 10.07; S, 10.52; Te, 20.59. Found: C, 54.40; H, 4.57; P, 10.02; S, 10.37; Te, 20.64%.

Acknowledgment

This work was supported by the Russian Foundation for Basic Research (grant N° . 11-03-00286) and the President of the Russian Federation (program for the support of leading scientific schools, grant NSh-1550.2012.3).

References

- N.K. Gusarova, B.A. Trofimov, A.A. Tatarinova, V.A. Potapov, A.V. Gusarov, S.V. Amosova, M.G. Voronkov, Zh. Org. Khim. (Russ.) 25 (1989) 39–45.
- [2] N.K. Gusarova, A.A. Tatarinova, L.M. Sinegovskaya, Sulfur Rep. 11 (1991) 1–50.
- [3] N.K. Gusarova, N.A. Chernysheva, S.V. Yas'ko, L.V. Klyba, B.A. Trofimov, Russ. J. Gen. Chem. 81 (2011) 2506–2509.
- [4] V.A. Potapov, M.V. Musalov, S.V. Amosova, M.V. Musalova, M.V. Penzik, Russ. J. Org. Chem. 47 (2011) 950–951.
- [5] B.A. Trofimov, N.K. Gusarova, A.A. Tatarinova, S.V. Amosova, V.M. Bzhezovskii, V.V. Shcherbakov, Zh. Org. Khim. (Russ.) 19 (1983) 457-458.
- [6] (a) N. Petragnani, H.A. Stefani, Tetrahedron 61 (2005) 1613–1679;
 (b) G. Zeni, D.S. Ludtke, R.B. Panatieri, A.L. Braga, Chem. Rev. 106 (2006)

1032–1076; (c) N. Petragnani, H.A. Stefani, Tellurium in Organic Synthesis, second ed.,

- Academic Press, 2007. [7] (a) J.M. Miller, J. Chem. Soc. A (1967) 828–834:
- (b) J.M. Milliams, R.S. Ward, R.G. Cooks, J. Am. Chem. Soc. 90 (1968) 966–972;
 (c) I. Granoth, J.B. Levy, C. Symmes, J. Chem. Soc. Perkin Trans. 2 (1972)

(d) A.T. Lebedev, Mass Spectrometry in Organic Chemistry. Izd, Binom,

Moscow, 2003 (in Russian); (e) A.T. Lebedev, K.S. Lebedev, B.F. Myasoedov, I.V. Rybal'chenko,

G.I. Sigeykin, V.N. Suvorkin, J. Mass Spectrom. 3 (2006) 277-283.

- [8] I. Granoth, The mass spectra of organophosphorus compounds, in: E.J. Griffith, M. Grayson (Eds.), Topics in Phosphorus Chemistry, vol. 8, John Wiley & Sons, New York, 1976, pp. 41–98.
- [9] Nist Mass Spectral Search Program NIST/EPA/NIH Mass Spectral Library/ Version 2.0d, Build Dec2005.
- [10] G. Baccolini, C. Boga, M. Mazzacurati, J. Org. Chem. 70 (2005) 4774-4777.
- [11] A.D. Becke, Phys. Rev. A 38 (1988) 3098-3100.
- [12] C.T. Lee, W.T. Yang, R.G. Parr, Phys. Rev. B 37 (1988) 785-789.
- [13] A.D. Becke, J. Chem. Phys. 98 (1993) 5648-5652.
- [14] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, V.G. Zakrzewski, J.A. Montgomery Jr., R.E. Stratmann, J.C. Burant, S. Dapprich, J.M. Millam, A.D. Daniels, K.N. Kudin, M.C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G.A. Petersson, P.Y. Ayala, Q. Cui, K. Morokuma, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J. Cioslowski, J.V. Ortiz, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P.M.W. Gill, B.G. Johnson, W. Chen, M.W. Wong, J.L. Andres, M. Head-Gordon, E.S. Replogle, J.A. Pople, Gaussian 98, Revision A.9, Gaussian, Inc., Pittsburgh, PA, 1998.