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Reaction of Divinyl Telluride with Secondary Phosphine Chalcogenides

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Abstract—Divinyl telluride reacted with 2 equiv of diphenylphosphine sulfide in the presence of AIBN as radical initiator (63–68°C) to give the corresponding anti-Markovnikov adduct in 68% yield with high regioselectivity. Treatment of the addition product with aqueous hydrogen peroxide at room temperature afforded 71% of vinyldiphenylphosphine oxide. Radical addition of diphenylphosphine selenide to divinyl telluride (AIBN, 63–68°C) led to the formation of 1,1,3,3-tetraphenyldiphosphoxane 1,3-diselenide in 82% yield.

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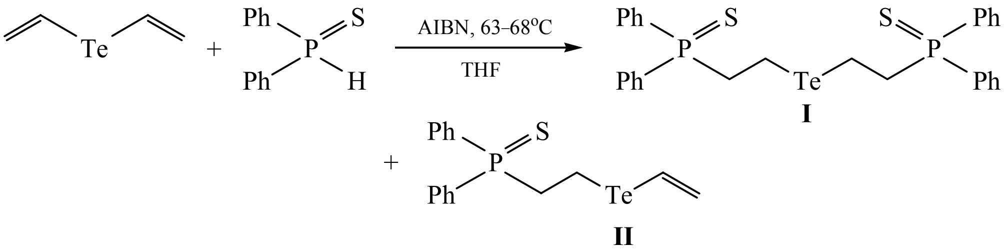
Chemistry of unsaturated organotellurium compounds vigorously develops [1–3]. Vinyl tellurides are efficient vinyl synthons for the preparation of natural compounds and their analogs [2, 4]. Vinyl tellurides were used to synthesize such pharmacologically important compounds as α,β-unsaturated δ-lactones [5], linear polyacetylenic acids [6], and (–)-macrolactin **A** [7].

Divinyl telluride is now among most promising and accessible unsaturated organotellurium reagents; it is readily available in quantitative yield from acetylene and elemental tellurium in aqueous potassium hydroxide in the presence of tin(II) chloride [8]. On the other hand, chemical transformations of divinyl telluride as promising building block for organic synthesis have been studied fairly poorly. It was reported that divinyl telluride takes up thiols under conditions of radical initiation [9], reacted with bromine to give divinyltellurium dibromide [9, 10], is converted into divinyl tellurone by the action of hydrogen peroxide [11], and takes up chalcogen dichlorides [9]. Reactions of divinyl telluride with PH compounds were not reported previously, though we recently described radical-initiated addition of secondary phosphine sulfides and phosphine selenides to alkyl vinyl tellurides [3].

In the present communication we report for the first time on the reaction of divinyl telluride with secondary phosphine chalcogenides. This reaction was studied with a view to obtain new data on the reactivity of these compounds, as well as to synthesize new tellurium- and -phosphorus-containing organic compounds.

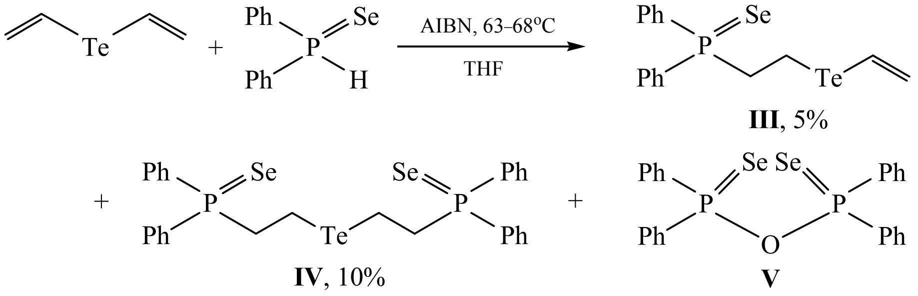
We have found that divinyl telluride reacts with diphenylphosphine sulfide at a molar ratio of 1:2.1 in the presence of azobis(isobutironitrile) (AIBN) as radical initiator at 63–68°C to give 2-[2-(diphenylphosphorothioyl)ethyl]tellanylethyl(diphenyl)phosphine



(1)

sulfide (**I**) as the major product (preparative yield 68%) and monoadduct **II** (~30% according to the NMR data). In the ^{1}H NMR spectrum of the product mixture, protons in the vinyl group of monoadduct **II** resonated at δ 5.71 (d, 1H, $=CH_2$, $^3J_{HH} = 17.6$ Hz), 6.05 (d, 1H, $=CH_2$, $^3J_{HH} = 10.3$ Hz), and 6.81 ppm (d.d, 1H, CH=). Compound **II** displayed in the mass spectrum the molecular ion peak (isotope cluster, *m/z* 402 for ^{130}Te) with an intensity of 5% of the total ion current.

The addition of secondary diphenylphosphine selenide to divinyl telluride under analogous conditions was characterized by low conversion: the overall yield of mono- and bis-adducts **III** and **IV** was as poor as ~15%. In this case, the major product was 1,1,3,3-tetraphenyldiphosphoxane 1,3-diselenide (**V**) which was isolated in 82% yield. Compound **V** is likely to be formed according to a scheme including oxidation of initial diphenylphosphine selenide to selenophopshinic acid **VI** and dehydration of the latter.



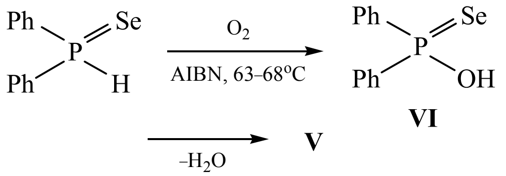
III, 5%

IV, 10%

V

(2)

The proposed scheme was confirmed experimentally. In fact, acid **VI** and its anhydride **V** were formed when diphenylphosphine selenide was heated on exposure to atmospheric oxygen (compounds **V** and **VI** were identified by ^{31}P NMR).

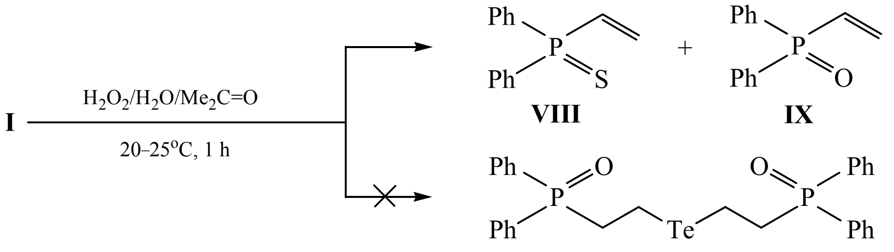


VI

V

(3)

Unlike secondary phosphine sulfides, diphenylphosphine oxide failed to react with divinyl telluride under analogous conditions (AIBN, 63–68°C) and remained intact. These findings are consistent with the known low reactivity of secondary phosphine oxides in radical processes [12]. Our attempt to obtain 2-[2-(diphenylphosphorothioyl)ethyl]tellanylethyl(diphenyl)-phosphine oxide (**VII**) by treatment of the corresponding phosphine sulfide **I** with 2 equiv of hydrogen peroxide led to unexpected results. Analysis of the reaction mixture by mass spectrometry revealed formation of two previously described compounds, diphenyl (vinyl)phosphine sulfide (**VIII**), *m/z* 244 (100%) $[M]^+$ [13], and diphenyl(vinyl)phosphine oxide (**IX**), *m/z* 228 (100) $[M]^+$ [14].



VIII

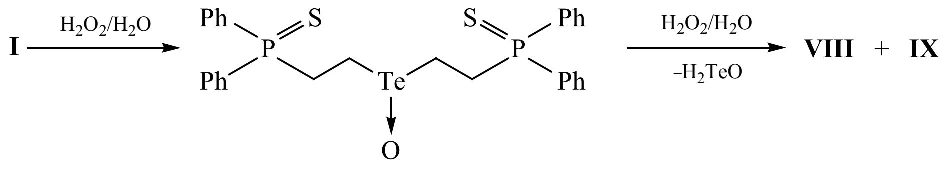
IX

VII

(4)

Presumably, the transformation of bis-adduct **I** by the action of hydrogen peroxide involves initial formation of intermediate telluroxide **A** which then characteristically undergoes elimination of TeO [15] to produce vinylphosphine chalcogenides **VIII** and **IX**. The subsequent treatment of phosphine chalcogenide mixture **VIII**/**IX** with hydrogen peroxide afforded pure diphenyl(vinyl)phosphine oxide (**IX**) in 71% yield.

To conclude, divinyl telluride was shown to be a convenient and accessible reagent for the synthesis of functionalized tellurium-containing bis(phosphine



A

(5)

sulfides) as promising multidentate ligands [16], as well as CH_2=CH synthon for the preparation of vinylphosphine oxides.

EXPERIMENTAL

The ^{1}H and ^{31}P NMR spectra were recorded on a Bruker DPX 400 spectrometer at 400.13 and 161.98 MHz, respectively, using C_6D_6 or $CDCl_3$ as solvent and 85% H_3PO_4 as external reference for ^{31}P. The IR spectra were measured in KBr on a Bruker IFS 25 spectrometer. The mass spectra (electron impact, 70 eV) were obtained on a Shimadzu GCMS-QP5050 instrument. All reactions were carried out under argon, and their progress was monitored by ^{31}P NMR spectroscopy.

2-[2-(Diphenylphosphorothioyl)ethyl]tellanylethyl(diphenyl)phosphine sulfide (I). A solution of 0.155 g (0.85 mmol) of divinyl telluride and 0.016 g (3%) of AIBN in 2 ml of tetrahydrofuran was flushed with argon and heated to 60°C under stirring using a magnetic stirrer, a solution of 0.39 g (1.79 mmol) of diphenylphosphine sulfide in 1 ml of THF was added dropwise, the mixture was stirred for 2.5 h at 63–68°C, and the solvent was removed under reduced pressure. The residue, 0.52 g of a bright yellow syrupy material (a mixture of compounds **I** and **II**), was treated with 5 ml of diethyl ether, the solvent was separated from the precipitate by decanting, and this procedure was repeated three times more. The precipitate was dried under reduced pressure. We thus isolated 0.36 g (68%) of bis-adduct **I**, white crystals, mp 146–150°C (from diethyl ether). IR spectrum (KBr), ν, cm^{-1}: 3052 ($C–H_{arom}$), 2931, 2902 (C–H), 1477 ($C=C_{arom}$), 1434, 1394 (δCH_2), 1310, 1248, 1180, 1154, 1139, 1102, 1069, 1026, 998, 928, 841, 762 ($\delta C–H_{arom}$), 752 sh (P–C), 744, 715, 706, 699 ($\delta C–H_{arom}$), 675, 623, 611, 603 (P=S), 589 (S–Te), 499, 486, 456, 430. ^{1}H NMR spectrum (C_6D_6), δ, ppm: 2.80 m (8H, CH_2), 7.07 m (12H, *m*-H, *p*-H), 7.93 m (8H, *o*-H). ^{31}P NMR spectrum (C_6D_6): δ_P 44.99 ppm. Found, %: C 54.62; H 4.47; P 10.07; S 10.52; Te 20.59. $C_{28}H_{28}P_2S_2Te$. Calculated, %: C 54.40; H 4.57; P 10.02; S 10.37; Te 20.64. *M* 618.2.

Reaction of divinyl telluride with diphenylphosphine selenide. A solution of 0.057 g (0.31 mmol) of divinyl telluride and 0.007 g (3%) of AIBN in 2 ml of THF was flushed with argon and heated to 60°C under stirring with a magnetic stirrer, a solution of 0.19 g (0.73 mmol) of diphenylphosphine selenide in 1 ml of THF was added dropwise, the mixture was stirred for 2.5 h at 63–68°C, and the solvent was removed under reduced pressure. The residue was treated with 3 ml of diethyl ether, the solvent was separated from the precipitate by decanting, and this procedure was repeated three times more. The precipitate was dried under reduced pressure. Yield of 1,1,3,3-tetraphenyldiphosphoxane 1,3-diselenide (**V**) 0.16 g (82%), colorless crystals, mp 175°C (from diethyl ether). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 7.35 m (8H, H_{arom}), 7.44 m (4H, H_{arom}), 7.84 m (8H, H_{arom}). ^{31}P NMR spectrum ($CDCl_3$): δ_P 82.91 ppm. Found, %: C 53.12; H 3.87; P 11.19; Se 29.22. $C_{24}H_{20}OP_2Se_2$. Calculated, %: C 52.97; H 3.70; P 11.38; Se 29.01. *M* 544.28. The physical constants and spectral parameters (^{1}H and ^{31}P NMR) of compound **V** were identical to those reported in [17]. The ether solution was concentrated under reduced pressure to isolate 0.08 g of a mixture of mono- and bis-adducts **III** and **IV**. ^{1}H NMR spectrum (C_6D_6), δ, ppm: 2.89 m (12H, CH_2), 5.72 d (1H, =CH_2, $^{3}J_{HH}$ = 17.8 Hz, **III**), 6.06 d (1H, =CH_2, $^{3}J_{HH}$ = 10.1 Hz, **III**), 6.82 d. d [1H, CH=, **III**), 7.02 m (18H, *m*-H, *p*-H), 7.78 m (4H, *o*-H, **III**), 7.93 m (8H, *o*-Ph, **IV**). ^{31}P NMR spectrum (C_6D_6), δ_P, ppm: 36.50 (**III**), 36.85 (**IV**).

Oxidation of 2-[2-(diphenylphosphorothioyl)ethyl]tellanylethyl(diphenyl)phosphine sulfide (I). Compound **I**, 0.2 g (0.32 mmol), was dissolved in 5 ml of acetone, 0.062 g (0.64 mmol) of 35% hydrogen peroxide was added, and the mixture was stirred for 1 h at room temperature on a magnetic stirrer (the consumption of hydrogen peroxide was qualitatively monitored by reaction with iodide ions). A white solid separated (~0.04 g) and was filtered off and washed in succession with water (3×1 ml) and acetone (2×0.5 ml). The filtrate was combined with the washings, adjusted to pH 8 by adding an aqueous solution of potassium carbonate, and extracted with chloroform (3 × 5 ml). The extract was dried over calcined K_2CO_3, the solvent was distilled off under reduced pressure, and the residue was dried in a vacuum; we thus isolated 0.11 g of an orange oil.

The product mixture was dissolved in 1 ml of acetone, and the solution was added to a solution containing 0.03 g (0.3 mmol) of hydrogen peroxide. The mixture was stirred for 1 h at room temperature on a magnetic stirrer, 1 ml of aqueous potassium carbonate was added to pH 8, the mixture was extracted with chloroform (3 × 3 ml), and the extract was dried over calcined K_2CO_3. The solvent was distilled off under reduced pressure, and the residue was dried in a vacuum. We thus isolated 0.105 g (71%) of diphenyl(vinyl)phosphine oxide (**IX**) as colorless crystals with mp 116°C (from ethyl acetate). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 6.20–6.36 m (2H, $=CH_2$), 6.58–6.72 m (1H, CH=), 7.46 m (6H, H_{arom}), 7.67 m (4H, H_{arom}). ^{31}P NMR spectrum ($CDCl_3$): δ_P 24.00 ppm. The product was identical to an authentic sample [18] in physical constants and spectral parameters (^{1}H and ^{31}P NMR).

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