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ScienceDirect
Mendeleev Commun., 2010, **20**, 346–347

Mendeleev Communications

Radical addition of secondary phosphine sulfides and selenides to vinyl tellurides

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DOI: 10.1016/j.mencom.2010.11.015

The regiospecific addition of secondary phosphine sulfide and phosphine selenide to alkyl vinyl tellurides proceeds under radical initiation (AIBN, 65–70 °C, 2.5–3.5 h) to afford the *anti*-Markovnikov adducts, (2-alkyltellanylethyl)phosphine chalcogenides, in 86–99% yields.

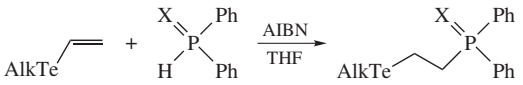
Tellurium reagents are used in various fields of synthetic organic chemistry[1] due to their chemo-, regio-, and stereoselectivity reactions. Organometallic complexes with tellurolato or tellanyl ligands are promising to design new materials for electronic devices.[1(*c*),2] The organotellurium compounds are known to be prospective pharmacological agents owing to their unique biological properties. Vinyl tellurides are also valuable intermediates in the synthesis of diverse natural products.[1(*c*),3]

Of special interest are functional organotellurium compounds including those bearing phosphorus-containing substituents. These compounds represent the reactive building blocks for organic and organoelement synthesis[1(*c*),4] as well as polydentate ligands for the design of metal-complex catalysts.[1(*c*),5] It has been also reported[6] that diethyl (*E*)-2-phenyl-2-(phenyltellanyl)-ethenylphosphonate possesses a high antioxidant activity and exerts neuroprotective action against Mn-induced neurotoxicity.

Therefore, the development of convenient approaches to the synthesis of phosphorus- and tellurium-containing compounds is an urgent research challenge. Apparently, among such approaches is the reaction of alkyl vinyl tellurides (readily prepared from acetylene, elemental tellurium and alkyl bromides[7]) with secondary phosphine chalcogenides.

The experiments have shown that pentyl vinyl and hexyl vinyl tellurides **1**, **2** react with diphenylphosphine sulfide **3** and diphenylphosphine selenide **4** under mild conditions [azobis-isobutyronitrile (AIBN), 65–70 °C, THF, 2.5–3.5 h] to give tertiary (2-alkyltellanylethyl)phosphine chalcogenides **5a–d** in 86–99% yields (Table 1).†

Table 1 Synthesis of tertiary (2-alkyltellanylethyl)phosphine chalcogenides **5a–d**.



1, **2** **3**, **4** **5a–d**

Vinyl telluride	Alk	$Ph_2P(X)H$	X	Time/h	Product	Yield (%)
1	C_5H_{11}	**3**	S	3.5	**5a**	99
1	C_5H_{11}	**4**	Se	3.5	**5b**	86
2	C_6H_{13}	**3**	S	3.0	**5c**	92
2	C_6H_{13}	**4**	Se	2.5	**5d**	87

In summary, the results obtained contribute to the understanding of reactivity of these compounds, provides a facile synthesis of new tertiary phosphine chalcogenides with alkyl telluride substituents and extends the synthetic potential of the reactions of PH-addends with alkenes. Such type of reactions represents one of the most convenient approaches to the C–P bond formation and continues to attract attention as a straightforward atom-economic ('green') route for the synthesis of tertiary phosphine chalcogenides, including functional ones.

† The ^1H and ^{31}P NMR spectra were measured on a Bruker DPX 400 (400.13 and 161.98 MHz, respectively) spectrometer. IR spectra were recorded on a Bruker IFS-25 spectrometer in thin layer. Mass spectra were obtained on a Shimadzu GCMS-QP5050A instrument; the energy of ionizing electrons was 70 eV, the temperature of the ion source was 200 °C. The samples were introduced into the ion source using a direct inlet system.

General procedure for the preparation of (2-alkyltellanylethyl)phosphine chalcogenides **5a–d**. A solution of vinyl telluride **1**, **2** (0.5 mmol) and phosphine chalcogenide **3**, **4** (0.5 mmol) in THF (4 ml) in the presence of AIBN (5 mass% from the total mass of reagents) was stirred under an argon atmosphere at 65–70 °C for 2.5–3.5 h. The reaction was monitored using ^{31}P NMR spectra that showed the disappearance of peaks of the starting secondary phosphine chalcogenide **3**, **4** at δ 7.70 and 23.03 ppm and the appearance of new peaks at 37.22–45.21 ppm corresponding to the products **5a–d**. The solution was passed through a thin layer of Al_2O_3. After solvent evaporation *in vacuo*, the products **5a–d** of analytical purity grade were obtained.

(2-Pentyltellanylethyl)(diphenyl)phosphine sulfide **5a**: dark orange oil, yield 0.22 g (99%). IR (ν/cm^{-1}): 3074, 3054 ($\nu_{=CH}$ of phenyl rings), 2956, 2924, 2869, 2856 (ν_{CH}), 1587, 1574, 1480 ($\nu_{C=C}$ of phenyl rings), 1464, 1436 (δ_{CH_2}), 1379 (δ_{CH_3}), 1334, 1309, 1263, 1229, 1181, 1159, 1141, 1104, 1069, 1028, 999, 749, 739 (δ_{CH} of phenyl rings), 711 ($\nu_{P–C}$), 692 (δ_{CH} of phenyl rings), 621 (sh), 609 ($\nu_{P=S}$), 501 ($\nu_{Te–C}$), 482. ^1H NMR ($CDCl_3$) δ: 0.86 (m, 3H, Me), 1.29 (m, 4H, CH_2CH_2Me), 1.71 (m, 2H, CH_2Pr), 2.65 (m, 2H, CH_2P), 2.76 (m, 2H, TeCH_2CH$_2$P), 2.87 (m, 2H, CH_2Bu), 7.46 (m, 6H, Ph), 7.82 (m, 4H, Ph). ^{31}P NMR ($CDCl_3$) δ: 45.21. MS, *m/z* (I_{TIC}, %): 446 (5) $[M]^+$ [calc. for $Ph_2P(^{32}S)CH_2CH_2{}^{130}TeC_5H_{11}$, 446]. Found (%): C, 51.67; H, 5.53; P, 6.92; S, 7.43; Te, 28.44. Calc. for $C_{19}H_{25}PSTe$ (%): C, 51.39; H, 5.67; P, 6.98; S, 7.22; Te, 28.74.

(2-Pentyltellanylethyl)(diphenyl)phosphine selenide **5b**: dark orange oil, yield 0.21 g (86%). IR (ν/cm^{-1}): 3074, 3054 ($\nu_{=CH}$ of phenyl rings), 2955, 2926, 2869, 2855 (ν_{CH}), 1588, 1573, 1483 ($\nu_{C=C}$ of phenyl rings), 1458, 1436 (δ_{CH_2}), 1378 (δ_{CH_3}), 1323, 1309, 1293, 1229, 1181, 1159, 1131, 1097, 1079, 1068, 1028, 999, 932 (sh), 917, 746 (δ_{CH} of phenyl rings), 703 (sh, $\nu_{P–C}$), 692 (δ_{CH} of phenyl rings), 618, 530 ($\nu_{P=Se}$), 506 ($\nu_{Te–C}$), 490. ^1H NMR ($CDCl_3$) δ: 0.86 (m, 3H, Me), 1.29 (m, 4H, CH_2CH_2Me), 1.71 (m, 2H, CH_2Pr), 2.66 (m, 2H, CH$_2$P), 2.75 (m, 2H, TeCH_2CH$_2$P), 2.98 (m, 2H, CH_2Bu), 7.41 (m, 6H, Ph), 7.83 (m, 4H, Ph). ^{31}P NMR ($CDCl_3$) δ: 37.22. Found (%): C, 46.21; H, 4.92; P, 6.42; Te, 25.59. Calc. for $C_{19}H_{25}PSeTe$ (%): C, 46.48; H, 5.13; P, 6.31; Se, 16.08; Te, 25.99.

This work has been carried out under financial support of leading scientific schools by the President of the Russian Federation (grant no. NSH-3230.2010.3).

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(2-Hexyltellanylethyl)(diphenyl)phosphine sulfide **5c**: dark orange oil, yield 0.21 g (92%). IR (ν/cm^{-1}): 3074, 3054 ($\nu_{=CH}$ of phenyl rings), 2955, 2924, 2869, 2853 (ν_{CH}), 1588, 1574, 1512, 1481 ($\nu_{C=C}$ of phenyl rings), 1464, 1436 (δ_{CH_2}), 1379 (δ_{CH_3}), 1333, 1309, 1276, 1240, 1215, 1189, 1158, 1142, 1105, 1069, 1028, 999, 978, 749 (sh), 733 (δ_{CH} of phenyl rings), 711 ($\nu_{P–C}$), 692 (δ_{CH} of phenyl rings), 621 (sh), 609 ($\nu_{P=S}$), 500 ($\nu_{Te–C}$), 483. ^{1}H NMR ($CDCl_3$) δ: 0.86 (m, 3H, Me), 1.26 [m, 6H, (C*H*$_2$)$_3$Me], 1.68 (m, 2H, C*H*$_2$Bu), 2.65 (m, 2H, C*H*$_2$P), 2.76 (m, 2H, TeC*H*$_2$CH$_2$P), 2.87 (m, 2H, C*H*$_2$C$_5$H$_{11}$), 7.48 (m, 6H, Ph), 7.82 (m, 4H, Ph). ^{31}P NMR ($CDCl_3$) δ: 44.53. MS, *m*/*z* (I_{TIC}, %): 375 (3) [M – C_6H_{13}]$^+$ [calc. for Ph$_2$P(^{32}S)CH$_2$CH$_2$^{130}TeC$_6$H$_{13}$, 460]. Found (%): C, 52.61; H, 6.08; P, 6.58; S, 6.93; Te, 27.50. Calc. for $C_{20}H_{27}PSTe$ (%): C, 52.44; H, 5.94; P, 6.76; S, 7.00; Te, 27.86.

(2-Hexyltellanylethyl)(diphenyl)phosphine selenide **5d**: dark orange oil, yield 0.22 g (87%). IR (ν/cm^{-1}): 3073, 3053 ($\nu_{=CH}$ of phenyl rings), 2955, 2924, 2853 (ν_{CH}), 1589, 1573, 1512, 1482 ($\nu_{C=C}$ of phenyl rings), 1464, 1436 (δ_{CH_2}), 1377 (δ_{CH_3}), 1334, 1308, 1277, 1237, 1216, 1184, 1160, 1142, 1100, 1069, 1027, 998, 976, 745 (δ_{CH} of phenyl rings), 710 (sh, $\nu_{P–C}$), 692 (δ_{CH} of phenyl rings), 618 (sh), 547, 530 ($\nu_{P=Se}$), 514 (sh), 490 ($\nu_{Te–C}$), 478. ^{1}H NMR ($CDCl_3$) δ: 0.87 (m, 3H, Me), 1.26 [m, 6H, (C*H*$_2$)$_3$Me], 1.69 (m, 2H, C*H*$_2$Bu), 2.66 (m, 2H, C*H*$_2$P), 2.75 (m, 2H, TeC*H*$_2$CH$_2$P), 2.99 (m, 2H, C*H*$_2$C$_5$H$_{11}$), 7.46 (m, 6H, Ph), 7.81 (m, 4H, Ph). ^{31}P NMR ($CDCl_3$) δ: 37.43. MS, *m*/*z* (I_{TIC}, %): 423 (3) [M – C_6H_{13}]$^+$ [calc. for Ph$_2$P(^{80}Se)CH$_2$CH$_2$^{130}TeC$_6$H$_{13}$, 508]. Found (%): C, 47.81; H, 5.53; P, 6.08; Te, 24.97. Calc. for $C_{20}H_{27}PSeTe$ (%): C, 47.57; H, 5.39; P, 6.13; Se, 15.64; Te, 25.27.

Received: 24th June 2010; Com. 10/3545