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LETTERS

# Synthesis and reaction of $\beta$ -organyltelluro vinylphosphonates and vinyl sulfones

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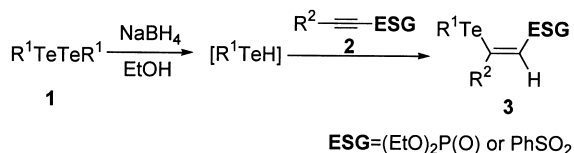
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## Abstract

Reactions of organyl tellurols generated in situ from ditellurides and alkynes bearing electron-stabilizing groups such as the phosphonyl and sulfonyl groups gave the  $\beta$ -organyltelluro vinylphosphonates or vinyl sulfones in high yield, which are followed by transmetallation by organometallic reagents. © 2000 Elsevier Science Ltd. All rights reserved.

*Keywords:* tellurium and compounds; transmetallation; phosphonic acids and derivatives; sulfones.

Hydrotelluration reactions of terminal unactivated alkynes are well-established<sup>1</sup> and the resulting compounds, vinyl tellurides, are known as useful intermediates of vinyl anion via a tellurium–metal exchange reaction,<sup>2</sup> whereas the internal alkyne cannot give this result. But, in the case of conjugated enynes, diynes,<sup>3</sup> alkynyl ketones, or esters,<sup>4</sup> hydrotelluration can give the corresponding vinyl telluride in good to excellent yields. To our knowledge, no result has been reported about the addition reactions of organyl tellurol to the alkynes bearing the electron stabilizing groups, such as phosphonate and sulfone.<sup>5</sup> Due to our recent interest related to the tellurium-based synthetic methodology,<sup>6</sup> herein we report the addition reaction of organyl tellurols to the alkynylphosphonates and alkynyl sulfones (Scheme 1, Table 1),<sup>7</sup> which are known by good



Scheme 1.

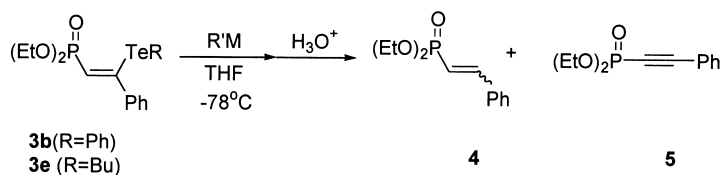
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Michael-acceptors.<sup>8</sup> It shows excellent yields of synthesis of stereoselective  $\beta$ -organytellurium substituted vinyl-phosphonates<sup>9</sup> and vinyl sulfones,<sup>10</sup> which are followed by further transmetallation. The resulting  $\beta$ -organytelluro vinylphosphonates and vinyl sulfones showed only *Z*-configuration (determined by NOE and NOESY).

Table 1  
Synthesis of vinylphosphonates and vinyl sulfones

ESG = phsophoryl			
R <sup>1</sup>	R <sup>2</sup>	Product	Yield (%)
Phenyl	H	<b>3a</b>	92
Phenyl	Phenyl	<b>3b</b>	95
Phenyl	Butyl	<b>3c</b>	94
Butyl	H	<b>3d</b>	85
Butyl	Phenyl	<b>3e</b>	72
Butyl	Butyl	<b>3f</b>	87
ESG =sulfonyl			
R <sup>1</sup>	R <sup>2</sup>	Product	Yield (%)
Phenyl	Phenyl	<b>3g</b>	93
Phenyl	Butyl	<b>3h</b>	94

Notably, in the case of compound **3e**, phenylethenylphosphonate was obtained as a side product (12% yield). When using an excess of [BuTeH] (generated from 1.0 mmol of (BuTe)<sub>2</sub> and 2.5 mmol of NaBH<sub>4</sub>) with **3e**, only phenylethenylphosphonate was produced in excellent yield (92%, only the *E* form).<sup>11</sup> Tellurium–metal exchange reaction was then investigated on **3b** and **3e** using *n*-butyllithium and Grignard reagent (Scheme 2, Table 2).

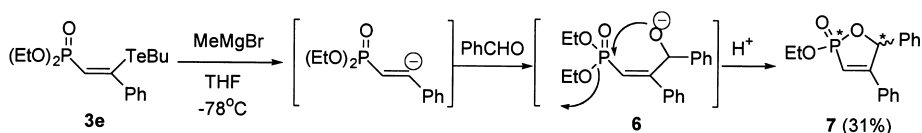


Scheme 2.

Table 2  
Transmetallation of **3b** and **3f**

R	R'M	Yield of <b>4</b> (%)	Yield of <b>5</b> (%)
Phenyl	<i>n</i> -BuLi	40 (E/Z= ~2:1)	30
Phenyl	<i>n</i> -BuLi-CeCl <sub>3</sub>	31 (E/Z= ~1:1)	24
Phenyl	EtMgBr	54 (only <i>E</i> )	10
Butyl	<i>n</i> -BuLi	61 (only <i>E</i> )	8
Butyl	EtMgBr	69 (only <i>E</i> )	-

$\beta$ -Phenyltelluro-phenylethenylphosphonate **3b** was treated with *n*-butyllithium in THF at  $-78^\circ\text{C}$  and then  $\text{H}_2\text{O}$  to give a *E*- and *Z*-2-phenylethenylphosphonate mixture (42%) and eliminated product, alkynylphosphonate, was obtained (30%). Before being transmetallated with the tellurium, *n*-butyllithium could act as a base on acidic  $\alpha$ -proton of vinylphosphonate. Also, it may affect the *E*:*Z* ratio of the produced vinylphosphonate. Using *n*-butyllithium– $\text{CeCl}_3$ <sup>12</sup> instead of *n*-butyllithium has given similar results. On the contrary, when using Grignard reagent, large amounts of *E*-2-phenylethenylphosphonate and relatively small amounts of alkynylphosphonate are produced. An improved result was shown in the case of  $\beta$ -butyltelluro-phenylethenylphosphonate **3e**. None of the alkynylphosphonate was obtained, and the yield was also enhanced. An interesting result was found on investigation of the substitution reaction of metallated vinylphosphonate with benzaldehyde to give cyclic product **7** (31%, Scheme 3).



Scheme 3.

The tendency for ring closure is so high that we cannot isolate the intermediate **6**. But using electrophiles such as acetyl chloride, ketones, and several alkyl halides, starting materials were recovered or complicated reaction mixtures were produced.

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- A typical reaction procedure for **3b** is as follows; Diphenylditelluride (0.205 g, 0.5 mmol) is added in a small portions under  $\text{N}_2$ , to a solution of  $\text{NaBH}_4$  (0.045 g, 1.2 mmol) in EtOH at room temperature. After 10 min a solution of phenylethynylphosphonate (0.262 g, 1.1 mmol) in EtOH (10 ml) is then added to the reaction mixture

- with stirring. After 10 h, the mixture is washed with saturated  $\text{NH}_4\text{Cl}$  solution, extracted with  $\text{Et}_2\text{O}$  ( $3 \times 20$  ml) and dried over  $\text{MgSO}_4$ . Evaporation of the solvent and purification by flash column chromatography on  $\text{SiO}_2$  (elution with hexane:EtOAc, 3:1) gives 2-phenyltelluro-2-phenylethynylphosphonate **3b** (0.422 g, 95%). Represented spectral data of  $\beta$ -organoyltellurovinylphosphonates. Compound **3b**:  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ )  $\delta$  1.39 (t, 6H,  $J=7.1$ ), 4.19 (quintet, 4H,  $J=7.3$ ), 6.39 (d, 1H,  $J=17.2$ ), 6.92 (m, 2H), 6.97 (s, 5H), 7.07 (m, 1H), 7.41 (m, 2H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  16.38 (d,  $J=6.2$ ), 62.02 (d,  $J=5.1$ ), 119.80 (d,  $J=189.8$ ), 127.22, 127.42, 127.56, 127.58, 127.60, 128.31, 140.37, 142.59 (d,  $J=24.7$ ), 153.47 (d,  $J=7.8$ ); HRMS (EI) calcd for  $\text{C}_{18}\text{H}_{21}\text{O}_3\text{P}\text{Te}$ : 446.0291, obs. 446.0263.  $\beta$ -Organoyltelluro vinyl sulfone **3g**:  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  6.84 (m, 3H), 6.90 (m, 5H), 7.05 (m, 1H), 7.36 (m, 2H), 7.58 (m, 2H), 7.66 (m, 1H), 8.07 (m, 2H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  111.96, 122.19, 122.33, 122.66, 122.92, 123.13, 123.49, 124.22, 124.52, 128.57, 134.51, 135.61, 135.77, 143.73. Cyclic phosphonate **7**: (\*# indicates the discernible peak of each diastereomer).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  1.25\* (t, 3H,  $J=7.1$ ), 1.31 (t, 3H,  $J=7.1$ ), 4.14 (m, 2H), 6.19 (m, 1H), 6.43 (m, 1H)\*, 7.24 (m, 10H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  16.31 (t,  $J=5.9$ ), 63.03 (d,  $J=6.4$ ), 83.33\* (d,  $J=8.3$ ), 83.50# (d,  $J=8.0$ ), 111.04# (d,  $J=167.3$ ), 111.30\* (d,  $J=170.18$ ), 126.82, 127.64#, 127.85\*, 128.53\*, 128.68#, 128.99#, 129.07\*, 130.09, 131.57\*, 131.64#, 131.93, 136.28\*, 136.31#, 160.76\*, 161.15# (d,  $J=18.8$ ); HRMS (EI) calcd for  $\text{C}_{17}\text{H}_{17}\text{O}_3\text{P}$ : 300.0915, obs. 300.0909.
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