



Pergamon

Tetrahedron Letters 41 (2000) 5103–5106

TETRAHEDRON
LETTERS

Synthesis and reaction of β -organyltelluro vinylphosphonates and vinyl sulfones

Won Bum Jang,^b Dong Young Oh^{b,*} and Chi-Wan Lee^{a,*}

^aDepartment of Chemistry, Center for Superfunctional Materials, Pohang University of Science and Technology, Pohang 790-784, South Korea

^bDepartment of Chemistry, Korea Advanced Institute of Science and Technology, Taejeon 305-701, South Korea

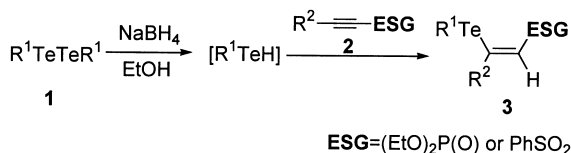
Received 12 April 2000; revised 9 May 2000; accepted 12 May 2000

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 β -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-established¹ and the resulting compounds, vinyl tellurides, are known as useful intermediates of vinyl anion via a tellurium–metal exchange reaction,² whereas the internal alkyne cannot give this result. But, in the case of conjugated enynes, diynes,³ alkynyl ketones, or esters,⁴ 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.⁵ Due to our recent interest related to the tellurium-based synthetic methodology,⁶ herein we report the addition reaction of organyl tellurols to the alkynylphosphonates and alkynyl sulfones (Scheme 1, Table 1),⁷ which are known by good



Scheme 1.

* Corresponding authors. Fax: 82-562-279-8137; e-mail: chiwan@chem.postech.ac.kr.

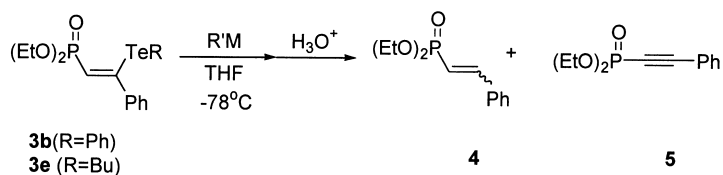
Michael-acceptors.⁸ It shows excellent yields of synthesis of stereoselective β -organyltellurium substituted vinyl-phosphonates⁹ and vinyl sulfones,¹⁰ which are followed by further transmetallation. The resulting β -organyltelluro vinylphosphonates and vinyl sulfones showed only *Z*-configuration (determined by NOE and NOESY).

Table 1
Synthesis of vinylphosphonates and vinyl sulfones

ESG = phosphoryl			
R ¹	R ²	Product	Yield (%)
Phenyl	H	3a	92
Phenyl	Phenyl	3b	95
Phenyl	Butyl	3c	94
Butyl	H	3d	85
Butyl	Phenyl	3e	72
Butyl	Butyl	3f	87

ESG = sulfonyl			
Phenyl	Phenyl	3g	93
Phenyl	Butyl	3h	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)₂ and 2.5 mmol of NaBH₄) with **3e**, only phenylethenylphosphonate was produced in excellent yield (92%, only the *E* form).¹¹ Tellurium–metal exchange reaction was then investigated on **3b** and **3e** using *n*-butyllithium and Grignard reagent (Scheme 2, Table 2).

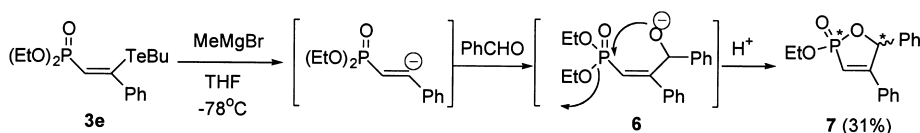


Scheme 2.

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

R	R'M	Yield of 4 (%)	Yield of 5 (%)
Phenyl	<i>n</i> -BuLi	40 (E/Z = ~2:1)	30
Phenyl	<i>n</i> -BuLi-CeCl ₃	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>)	-

β -Phenyltelluro-phenylethenylphosphonate **3b** was treated with *n*-butyllithium in THF at -78°C and then H_2O 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 α -proton of vinylphosphonate. Also, it may affect the *E*:*Z* ratio of the produced vinylphosphonate. Using *n*-butyllithium– CeCl_3 ¹² 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 β -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.

References

- (a) Tucci, F. C.; Chieffi, A.; Comasseto, J. V.; Marino, J. P. *J. Org. Chem.* **1996**, *61*, 4975; (b) Comasseto, J. V.; Ling, L. W.; Petragnani, N.; Stefani, H. A. *Synthesis* **1997**, 373; (c) Dabdoub, M. J.; Dabdoub, V. B.; Comasseto, J. V.; Petragnani, N. *J. Organomet. Chem.* **1986**, *308*, 211; (d) Takahashi, H.; Ohe, K.; Uemura, S.; Sugita, N. *Nippon Kagaku Kaishi* **1987**, 1508; (e) Ohe, K.; Takahashi, H.; Uemura, S.; Sugita, N. *J. Org. Chem.* **1987**, *52*, 4859; (f) Uemura, S.; Fukuzawa, S. I.; Patil, S. R. *J. Organomet. Chem.* **1983**, *243*, 9; (g) Barros, S. M.; Dabdoub, M. J.; Dabdoub, V. M. B.; Comasseto, J. V. *Organometallics* **1989**, *8*, 1661.
- Petragnani, N. In *Tellurium in Organic Synthesis*; Academic Press: London, 1994; pp. 216.
- (a) Dabdoub, M. J.; Dabdoub, V. B.; Comasseto, J. V. *Tetrahedron Lett.* **1992**, *33*, 2261; (b) Zeni, G.; Formiga, H. B.; Comasseto, J. V. *Tetrahedron Lett.* **2000**, *41*, 1311.
- (a) Detty, M. R.; Murray, B. J.; Smith, D. L.; Zumbulyadis, N. *J. Am. Chem. Soc.* **1983**, *105*, 875; (b) Detty, M. R.; Luss, H. R.; Mckelvey, J. M.; Geer, S. M. *J. Org. Chem.* **1986**, *51*, 1692; (c) Mo, X.-S.; Huang, Y.-Z. *Tetrahedron Lett.* **1995**, *36*, 3539; (d) Buzilova, S. R.; Sadekov, I. D.; Lipovich, T. L.; Filippova, T. M.; Vereschagin, L. I. *Zh. Obshch. Khim.* **1977**, *47*, 1999.
- During the preparation of the present manuscript, Brazilian authors published the reaction of sodium organyl chalcogenolates to alkynylphosphonates, however, which does not include sulfone moiety and further transmetallation using the resulting tellurides: Braga, A. L.; Alves, E. F.; Silveira, C. C.; de Andrade, L. H. *Tetrahedron Lett.* **2000**, *41*, 161.
- (a) Lee, C.-W.; Koh, Y. J.; Oh, D. Y. *J. Chem. Soc. Perkin Trans. I* **1994**, 717; (b) Sung, J. W.; Lee, C.-W.; Oh, D. Y. *Tetrahedron Lett.* **1995**, *36*, 1503; (c) Sung, J. W.; Jang, W. B.; Oh, D. Y. *Tetrahedron Lett.* **1996**, *37*, 7537; (d) Sung, J. W.; Park, C. P.; Gil, J. M.; Oh, D. Y. *J. Chem. Soc. Perkin Trans. I* **1997**, 591; (e) Park, C. P.; Sung, J. W.; Oh, D. Y. *Synlett* **1999**, 1055.
- A typical reaction procedure for **3b** is as follows; Diphenylditelluride (0.205 g, 0.5 mmol) is added in a small portions under N_2 , to a solution of 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 NH_4Cl solution, extracted with Et_2O (3×20 ml) and dried over MgSO_4 . Evaporation of the solvent and purification by flash column chromatography on SiO_2 (elution with hexane: EtOAc , 3:1) gives 2-phenyltelluro-2-phenylethenylphosphonate **3b** (0.422 g, 95%). Represented spectral data of β -organyltellurovinylphosphonates. Compound **3b**: ^1H NMR (200 MHz, CDCl_3) δ 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}C NMR (75 MHz, CDCl_3) δ 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 $\text{C}_{18}\text{H}_{21}\text{O}_3\text{PTe}$: 446.0291, obs. 446.0263. β -Organyltelluro vinyl sulfone **3g**: ^1H NMR (300 MHz, CDCl_3) δ 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}C NMR (75 MHz, CDCl_3) δ 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). ^1H NMR (300 MHz, CDCl_3) δ 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}C NMR (75 MHz, CDCl_3) δ 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.

8. Perlmutter, P. In *Conjugate Addition Reactions in Organic Synthesis*, 1st ed.; Pergamon Press: Oxford, 1992; Chapter 7.
9. For a review on vinyl phosphonate, see: Minami, T.; Motoyoshiya, J. *Synthesis* **1992**, 333.
10. Simpkins, N. S. In *Sulphones in Organic Synthesis*, 1st Ed.; Pergamon Press: Oxford, 1993; Chapter 4.
11. Terminal acetylene has been fully reduced in this condition. See: Aso, Y.; Nishioka, T.; Osuka, M.; Nagakawa, K.; Sasaki, K.; Otsubo, T.; Ogura, F. *Nippon Kagaku Kaishi* **1987**, 1490.
12. (a) Imamoto, T.; Takiyama, N.; Nakamura, K.; Hatajima, T.; Kamiya, Y. *J. Am. Chem. Soc.* **1989**, *111*, 4392; (b) Bartoli, G.; Marcantoni, E.; Sambri, L.; Tamburini, M. *Angew., Chem. Int. Ed. Engl.* **1995**, *34*, 2046.