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# Stereoselective addition of sodium organyl chalcogenolates to alkynylphosphonates: synthesis of diethyl 2-(organyl)-2-(organochalcogenyl)vinylphosphonates

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## Abstract

Organyl thiolate, selenolate or tellurolate anions reacted with alkynylphosphonates **1** to give diethyl 2-(organyl)-2-(organochalcogenyl)vinylphosphonates [β-organochalcogenyl vinylphosphonates] **2** in satisfactory yields. The reaction was stereoselective, giving predominantly or exclusively the (*Z*)-stereoisomer. © 1999 Elsevier Science Ltd. All rights reserved.

In the last few decades, there has been remarkable interest in the synthesis of vinylic chalcogenides and their synthetic applications.[1a] Diethyl 2-(organyl)-2-(organochalcogenyl)vinylphosphonates [β-organochalcogenyl vinylphosphonates] **2** are intermediates of great synthetic potential since they combine the well-known chemical reactivity of vinylic chalcogenides[1a] and vinylic phosphonates.[1b] The selenium derivatives were recently prepared by Pd-mediated stereoselective selenophosphorylation of alkynes.[2]

Hydrometallation of acetylenes is a widely used method for the synthesis of vinylic metal and metalloid derivatives.[1a] In this communication we describe a new, general and stereoselective method to synthesize β-organochalcogenyl vinylphosphonates **2** by means of the hydrochalcogenation of diethyl 1-alkynylphosphonates **1**.

We started our investigations with the hydrotelluration of alkynylphosphonates.[3] The reaction was performed by addition of alkynylphosphonates to a solution of sodium organyl tellurolate, prepared by reduction of diorganyl ditellurides with sodium borohydride in ethanol at room temperature[4] (Scheme 1). The β-organotelluranyl vinylphosphonates were formed in satisfactory yields with total regio- and *Z*-stereoselectivity (Table 1). The same procedure was used for the synthesis of β-organosulfanyl and organoselanyl vinylphosphonates. However, in these cases, the stereoselectivity was lower than for the tellurium analogues, probably as a result of the lower nucleophilicity of the organyl thiolate and selenolate anion. In all cases studied, only the regioisomer shown in Scheme 1 was obtained. This result can be

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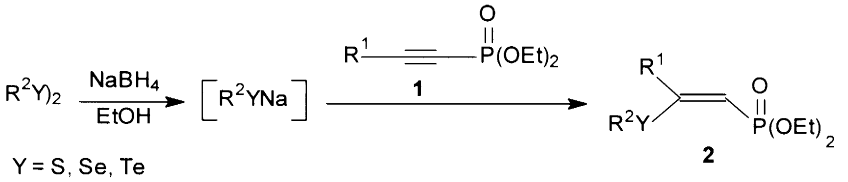
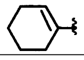
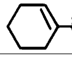
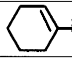
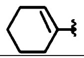
rationalized in terms of a Michael-type addition with carbanion stabilization by the diethoxyphosphinyl group.[1b]



Scheme 1.

Table 1
Preparation of diethyl 2-(organyl)-2-(organochalcogenyl)vinylphosphonates **2**

| $(R^2Y)_2$ | $R^1$ | time (h) | *E*:*Z*[b] | Yield (%)[a] | $(R^2Y)_2$ | $R^1$ | time (h) | *E*:*Z*[b] | Yield (%)[a] |
|---|---|---|---|---|---|---|---|---|---|
| $(PhTe)_2$ | Ph | 4 | 0:100 | 69 | $(PhSe)_2$ | *n*-Bu | 22 | 0:100 | 33 |
| $(PhTe)_2$ | *n*-Bu | 5 | 0:100 | 60 | $(PhSe)_2$ |  | 19 | 0:100 | 26 |
| $(PhTe)_2$ |  | 5 | 0:100 | 41 | $(n\text{-}BuSe)_2$ | Ph | 21 | 37:63 | 68 |
| $(n\text{-}BuTe)_2$ | Ph | 4 | 0:100 | 50 | $(n\text{-}BuSe)_2$ | *n*-Bu | 22 | 28:72 | 70 |
| $(n\text{-}BuTe)_2$ | *n*-Bu | 5 | 0:100 | 49 | $(PhS)_2$ | *n*-Bu | 21 | 0:100 | 46 |
| $(n\text{-}BuTe)_2$ |  | 4 | 0:100 | 42 | $(PhS)_2$ | Ph | 19 | 30:70 | 57 |
| $(PhSe)_2$ | Ph | 21 | 0:100 | 40 | $(PhS)_2$ |  | 19 | 0:100 | 34 |

[a] Isolated yields. [b] The ratios of *E*- and *Z*-isomers were estimated on the basis of $^1H$ NMR data.

The exclusive *Z*-stereochemistry was expected by analogy with the hydrotelluration of acetylenes.[5] These configurations were confirmed by NMR spectral analysis, especially NOESY experiments, for all the compounds **2.**

In summary, a novel method for the synthesis of diethyl 2-(organyl)-2-(organochalcogenyl)vinylphosphonates **2** has been established. It is expected that the reactions described above will find considerable application in organic synthesis.

## Acknowledgements

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## References

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2. Tanaka, M.; Choi, N.; Han, L. *J. Am. Chem. Soc.* **1996**, *118*, 7000.
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4. Typical procedure: To a solution of RYNa [generated in situ from $R^2YYR^2$ (1.0 mmol) and $NaBH_4$ (2.2 mmol)] in absolute ethanol (10 mL) the 1-alkynylphosphonate **1** (2.0 mmol) was added dropwise at room temperature. The reaction mixture was

stirred for the time indicated in Table 1. Then the mixture was poured into a saturated aqueous solution of $NH_4Cl$ (10 mL) and the aqueous layer was extracted with ethyl acetate (2×25 mL). The organic layer was dried ($MgSO_4$) and evaporated. The residue was purified by flash chromatography on silica gel with ethyl acetate:hexane (3:7). Selected spectral and analytical data for **2** ($R^2Y$=PhTe; $R^1$=*n*-Bu): $^1H$ NMR (200 MHz, $CDCl_3$): $\delta$ 7.92 (d, $J$=7.6 Hz, 2H), 7.42–7.21 (m, 3H), 6.27 (d, $^2J_{P\text{–}H}$=16.4 Hz, 1H), 4.11 (dq, $^3J_{P\text{–}H}$=7.5 Hz, $J$=7.2 Hz, 4H), 2.21 (t, $J$=7.8 Hz, 2H), 1.40–1.23 (m, 2H), 1.35 (t, $J$=7.2 Hz, 6H), 1.00 (sext, $J$=7.4 Hz, 2H), 0.66 (t, $J$=7 Hz, 3H); $^{13}C$ NMR (50 MHz, $CDCl_3$) $\delta$ 154.75 (d, $^2J_{P\text{–}C}$=6.3 Hz), 141.43, 128.58, 128.27, 115.33 (d, $^1J_{P\text{–}C}$=192 Hz), 115.29, 61.27 (d, $^2J_{P\text{–}C}$=5 Hz), 41.67 (d, $^3J_{P\text{–}C}$=23 Hz), 31.56, 21.16, 15.94 (d, $^3J_{P\text{–}C}$=6.2 Hz), 13.05; $^{31}P$ NMR (161 MHz, $CDCl_3$) $\delta$ 15.33 (s); MS *m/z* (relative intensity) 426 (M+2, 25), 347 (15), 219 (76), 163 (80), 81 (100); IR (KBr, film; $cm^{-1}$) 3064, 2956, 1559, 1433, 1391, 1292, 1231, 1163, 1027, 965. Anal. calcd for $C_{16}H_{25}O_3PTe$: C, 45.33; H, 5.94. Found: C, 44.91; H, 5.80.

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