

Preparation of 1-Telluroalkylphosphonates: New Synthetic Route to Vinyl Tellurides

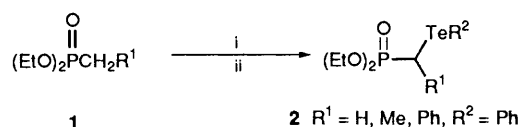
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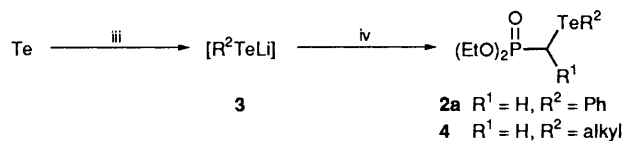
Reactions of the lithio anions derived from diethyl alkylphosphonates **1** with benzenetellurenyl iodide **5** give diethyl 1-(phenyltelluro)alkylphosphonates **2**. Diethyl (alkyltelluromethyl)phosphonates **4** are prepared by the treatment of lithium tellurolates **3** with iodomethylphosphonates **6**. (Phenyltelluromethyl)phosphonate and NaH reacted with aldehydes to produce vinyl tellurides **7**.

In recent years, the development of a large number of tellurium-based synthetic methods has made significant contributions to synthetic organic chemistry.¹ Recently, we reported our results on the synthesis of ketene selenoacetals from [bis(phenylseleno)methyl]phosphonate with aldehydes and ketones.² As an extension of this reaction we investigated a new route to vinyl tellurides. Vinyl tellurides are among the classes of organotellurium reagents with expected synthetic utility,¹ by analogy with a large range of well established transformations of similar selenium derivatives. Vinyl tellurides as well as other diorganyl tellurides undergo facile transmetalation with organolithiums³ and transition metal complexes,⁴ and have great potential in organic synthesis. In a recent report Han *et al.* have described a new synthesis of vinyl tellurides by carbottelluration of alkynes.⁵ In this paper, we report a facile method for the synthesis of vinyl tellurides **7** having predominantly the *E* configuration by a Wadsworth–Emmons reaction⁶ of tellurophosphonates with aldehydes. Although dialkyl 1-(alkylthio)-, 1-(arylthio)-alkylphosphonates⁷ and dialkyl 1-(arylseleno)alkylphosphonates⁸ are readily available by well established methods, the preparation of tellurophosphonates has not previously been reported. So we have developed two new methods for the preparation of diethyl 1-(phenyltelluro)alkylphosphonates **2** and diethyl (alkyltelluromethyl)phosphonates **4** as shown in Scheme 1. The results are summarized in Table 1.

Method A:



Method B:



Scheme 1 i, LDA, THF, -78°C ; ii, PhTeI **5**; iii, R^2Li , THF, 0°C ; iv, $(\text{EtO})_2\text{P}(\text{O})\text{CH}_2\text{I}$ **6**

Areneselenenyl halides are versatile reagents which have been widely used in organic synthesis.⁹ However, applications of arenetellurenyl halides¹⁰ are quite limited. Considering the lack of methods for the preparation of tellurophosphonates, we tried to utilize the electrophilicity of benzenetellurenyl iodide **5**,¹¹ by allowing it to react with lithio alkylphosphonates; this proved to be a convenient method for the synthesis of 1-(phenyltelluro)alkylphosphonates **2** (method A).

Table 1 Preparation of the 1-telluroalkylphosphonates $(\text{EtO})_2\text{P}(\text{O})\text{CHR}^1\text{R}^2$ **2** and **4**

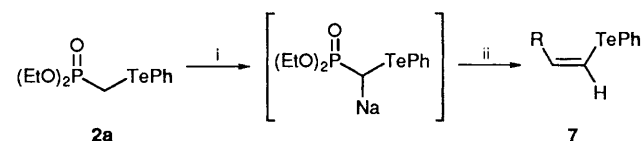
	Product		Method	Yield (%) ^a
	R ¹	R ²		
2a	H	TePh	A	90
2b	Me	TePh	A	76
2c	Ph	TePh	A	65
2a	H	TePh	B	77
4a	H	TeBu	B	62
4b	H	TeC≡CBu	B	51
4c	H	TeMe ₃ SiCH ₂	B	60

^a Isolated yields.

As reported by other workers,¹² we found that elemental tellurium readily inserted into the C–Li bond of organolithium reagents to form the organotellurolates **3**.¹³ These organotellurolates reacted with diethyl iodomethylphosphonate **6** to give diethyl (alkyltelluromethyl)phosphonates **4** in moderate yields (method B).

In method A, when 1 equiv. of lithium diisopropylamide (LDA) was used, the lithiated diethyl alkylphosphonate **1** formed was quenched by proton transfer from the 1-(phenyltelluro)alkylphosphonates **2** initially formed. In method B, we found that less of the tellurophosphonates was obtained at reflux than at -78°C . For example, the reaction of the lithium benzenetellurolate with diethyl iodomethylphosphonate **6** at -78°C gave tellurophosphonate **2a** in 77% yield. However, when carried out, at reflux the reaction yield was 35%.

In the synthesis of vinyl tellurides, it is possible for the lithium reagent to abstract the phenyltellurenyl moiety of **2a** by a Te–Li exchange reaction,³ so we used NaH as a base instead. A general reaction scheme is shown in Scheme 2 and the results are summarized in Table 2.



Scheme 2 Reagents and conditions: i, NaH, THF, room temp.; ii, RCHO, reflux

Experimental

¹H NMR spectra were obtained on Bruker AM-200 and AM-300 spectrometers, chemical shifts are quoted in ppm downfield from tetramethylsilane as an internal standard and *J* values are

Table 2 Synthesis of vinyl tellurides 7

Entry	RCHO	Product ^a	Yield (%) ^b
7a	PhCHO	PhCH ^E CHTePh	95
7b	<i>m</i> -NO ₂ C ₆ H ₄ CHO	<i>m</i> -O ₂ NC ₆ H ₄ CH ^E CHTePh	92
7c	<i>p</i> -ClC ₆ H ₄ CHO	<i>p</i> -ClC ₆ H ₄ CH ^E CHTePh	83
7d	2-FurylCHO	2-FurylCH ^E CHTePh	94
7e	PhCH ^E CHCHO	PhCH ^E CHCH ^E CHTePh	82

^a All the compounds were fully characterized. Vinyl tellurides **7a–d** have the *E* configuration as J_{HH} across the double bond is 16.5–16.8 Hz. Diaryl telluride **7e** is presumably *EE*, but only one J_{HH} of 14.9 Hz could be measured. The *E* configuration is expected from analogous chemistry.¹⁶ ^b Isolated yield.

given in Hz. Mass spectra were obtained on a Hewlett Packard 5985A GC–MS system using the electron impact (EI) method. Analytical thin layer chromatograph (TLC) was performed on precoated glass plates (0.25 mm) coated with silica gel 60 GF₂₅₄ (E. Merck). Preparative thin layer chromatography was carried out on silica gel, Merck 60 GF₂₅₄, 20 × 20 cm glass plates with 0.5 mm thickness. The plates were activated by heating in an oven at 125 °C overnight. Reagent grade chemicals, which were purchased from Aldrich, Sigma, and the Fluka Chemical Company, were used without further purification. The organic solvents were obtained from Wako Pure Chemical Industries Ltd., Duksan Pharmaceutical Company Ltd. and Junsei Chemical Company. Tetrahydrofuran (THF) was dried by refluxing over sodium–benzophenone for 5 h. Diphenyl ditelluride¹⁴ and iodomethylphosphonate¹⁵ were prepared according to the literature.

Preparation of 1-(Phenyltelluro)alkylphosphonates 2 (Method A).—To a stirred solution of LDA (2.0 mmol in 3 cm³ THF) was added diethyl phosphonate **1** (1 mmol in 2 cm³ THF) at –78 °C under a nitrogen atmosphere. After the mixture had been stirred for 1 h at the same temperature, benzenetellurenyl iodide **5** [1 mmol in 3 cm³ of THF; prepared *in situ* by the addition of iodine (0.5 mmol) solution in dry THF (2 cm³) dropwise to a stirred solution of diphenyl ditelluride (0.5 mmol) in dry THF (1 cm³), followed by stirring for 2 h] was added. The dark brownish colour turned to pale yellow immediately. After 1 h, the reaction mixture was warmed to room temp. for 1 h. Then, sat. aq. NH₄Cl was added and the mixture was extracted with diethyl ether. The organic extract was dried (MgSO₄) and evaporated to give 1-(phenyltelluro)alkylphosphonates **2**, which were purified by column chromatography on silica-gel with ethyl acetate–hexane (1:1). **2a**, δ_{H} (300 MHz; CDCl₃) 1.30 (t, 6 H, *J* 7), 3.00 (d, 2 H, *J* 12.8), 4.12 (quintet, 4 H, *J* 7) and 7.20–7.84 (m, 5 H); δ_{C} (CDCl₃) –3.84 (d, *J* 150.68), 16.33 (d, *J* 6.15), 62.55 (d, *J* 6.52), 112.11 (d, *J* 3.38), 128.24, 129.29 and 138.54; δ_{P} 27.90; m/z 358 [M⁺, 36.8%, ¹³⁰Te]; **2b**, δ_{H} (200 MHz; CDCl₃) 1.34 (t, 6 H, *J* 7), 1.76 (dd, 3 H, *J* 7.5, 18.16), 3.3 (dq, 1 H, *J* 7, 14), 4.1 (m, 4 H) and 7.1–7.9 (m, 5 H); m/e 372 (M⁺, 56.8%, ¹³⁰Te); **2c**, δ_{H} (200 MHz; CDCl₃) 1.25 (t, 6 H, *J* 7), 4.09–4.19 (m, 5 H) and 7.2–8.2 (m, 10 H).

Preparation of (Phenyltelluromethyl)phosphonates 2a and (Alkyltelluromethyl)phosphonates 4 (Method B).—Tellurium powder (1 mmol) and freshly distilled THF (2 cm³) were placed in a two-necked flask under a nitrogen atmosphere. The mixture was chilled to 0 °C with an ice bath and the organolithium reagent (1 mmol) was added dropwise. If the solution was dark brown after 0.5 h, a few more drops of organolithium were added until the solution lightened. The resulting light brown or yellow solution was then chilled to –78 °C, and iodomethylphosphonate **6** (1 mmol) was added as a neat liquid *via* a syringe. The reaction mixture was quenched with sat. aq.

NH₄Cl, and extracted with diethyl ether. The organic layer was isolated and dried over MgSO₄. The resulting solution was filtered, followed by concentration and column chromatography to afford (alkyltelluromethyl)phosphonates **4**. **4a**, δ_{H} (200 MHz; CDCl₃) 0.92 (t, 3 H, *J* 7), 1.39 (m, 8 H), 1.77 (quintet, 2 H, *J* 7), 2.67 (d, 2 H, *J* 12.8), 2.85 (t, 2 H, *J* 7) and 4.11 (quintet, 4 H, *J* 7); m/e 338 (M⁺, 7.0%, ¹³⁰Te); **4b**, δ_{H} (200 MHz; CDCl₃) 0.92 (t, 3 H, *J* 7), 1.39 (m, 10 H), 2.5 (t, 2 H), 3.04 (d, 2 H, *J* 12.7) and 4.17 (quintet, 4 H); m/z 362 (M⁺, 3.6%, ¹³⁰Te); **4c**, δ_{H} (200 MHz; CDCl₃) 1.24 (t, 6 H, *J* 7), 1.97 (s, 2 H), 2.59 (d, 2 H, *J* 12.8) and 4.1 (quintet, 4 H, *J* 7).

Preparation of Vinyl Tellurides 7.—To a mixture of NaH (1 mmol) (80% suspension in oil) and (phenyltelluromethyl)phosphonate **2a** (1 mmol) in THF (5 cm³) at reflux under N₂, aldehydes (1 mmol) was added dropwise. Following 3 h at reflux, the solution was cooled to room temperature. Then, sat. aq. NH₄Cl was added and the mixture was extracted with diethyl ether. The organic extract was dried (MgSO₄) and evaporated to give vinyl tellurides, which were purified by column chromatography on silica gel with ethyl acetate–hexane (1:20) or by preparative thin layer chromatography. **7a**, δ_{H} (200 MHz; CDCl₂) 7.20 (d, 1 H, *J* 16.6), 7.39 (m, 8 H), 7.64 (d, 1 H, *J* 16.6) and 7.83 (m, 2 H); m/e 310 (M⁺, 22.6%, ¹³⁰Te); **7b**, δ_{H} (200 MHz; CDCl₃) 6.96 (d, 1 H, *J* 16.8) and 7.40–8.05 (m, 10 H); m/e 355 (M⁺, 21.0%, ¹³⁰Te); **7c**, δ_{H} (200 MHz; CDCl₃) 6.99 (d, 1 H, *J* 16.7), 7.25 (m, 7 H), 7.52 (d, 1 H, *J* 16.7) and 7.75 (m, 2 H); m/z 344 (M⁺, 6.1%, ¹³⁰Te); **7d**, δ_{H} (200 MHz; CDCl₃) 6.15 (m, 1 H), 6.35 (m, 1 H), 6.84 (d, 1 H, *J* 16.5), 7.25–7.34 (m, 4 H), 7.43 (d, 1 H, *J* 16.5) and 7.74 (m, 2 H); m/e 300 (M⁺, 16.1, ¹³⁰Te); **7e**, δ_{H} (200 MHz; CDCl₃) 6.43 (d, 1 H, *J* 14.9), 6.95–7.38 (m, 10 H) and 7.71–7.82 (m, 3 H); m/e 336 (M, 4.5%, ¹³⁰Te).

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