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Preparation of symmetrical divinyl tellurides via an ylidation reaction

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Abstract

Symmetrical divinyl tellurides are prepared by sequential reaction of bis-(triphenylmethyl phosphonium) halotellurate with base or by the reaction of triphenylmethylidene phosphoranes with TeCl₄, followed by aldehydes. The products are converted to E- α , β -unsaturated aldehydes by treatment with *n*-BuLi and DMF. © 1999 Elsevier Science S.A. All rights reserved.

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1. Introduction

Tellurium compounds have recently attained a remarkable development as synthetic reagents and intermediates [1]. Among the many classes of organotellurium compounds, vinylic tellurides play an important role [2], justifying a recent review concerning their preparation and reactivity [3].

The most important synthetic applications of vinylic tellurides are certainly the detellurative coupling reactions and the transmetalation reaction, i.e. the substitution of the tellurium moiety by the organic moiety of different organocuprates [4], and the Li/Te or Cu/Te exchange giving, respectively, vinyllithium [5] or vinyl-copper reagents [6].

Symmetrical divinyl tellurides are especially useful in transmetalation reactions since by treating them with two equivalents of Li or copper reagents, both of the vinyl groups are displaced. This process occurs with retention of the carbon–carbon bond geometry and the resulting Li derivative can be trapped by a variety of electrophiles.



A straightforward method for the preparation of symmetrical divinyl tellurides is based on the hydrotelluration of acetylenes with the system $Te/NaBH_4/$ EtOH, THF/aq NaOH [6a]. However, this method, which produces predominantly Z adducts, works well only with acetylenes conjugated to aryl groups, C=C double bonds or other electron-withdrawing groups. By contrast, alkylacetylenes are fairly unreactive, in accordance with the unsatisfactory results described for the addition of organotellurolates to these acetylenes [5b,6].

$$2 R \longrightarrow H \xrightarrow{\text{Te, NaBH_4, EtOH, THF}} R \xrightarrow{\text{Te}} R$$

2. Results and discussion

New methods for the preparation of symmetrical divinyl tellurides deserve additional efforts. In this paper we describe the preparation of these compounds in

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accordance with the approach previously reported by us for the preparation of arylvinyl tellurides [7] employing aryltellurophosphoranes. The method consists in the sequential treatment of bis-(triphenylmethylphosphonium) halotellurate [8] 1 with excess of base (six equivalents LICA-lithium dicyclohexylamide) and then with the aldehyde in THF at -78° C. This sequence involves the step by step deprotonation of 1, generating the bis-dichlorotellurophosphonium salt 2 and in sequence the bis-dichlorotellurophosphorane 3. Reaction with two equivalents of the aldehyde should have produced the divinyl tellurium dichloride 4. However, 4 was not isolated and instead, the divinyltelluride 8 was obtained [9]. This intriguing result can be rationalized on the basis of the known reaction of phosphoranes with dihalogen sources giving α -haloalkyl/phosphonium halides [10]. Once 3 is formed, it suffers dehalogenation by disproportionation to give the bis-tellurophosphorane 5 and mono-chloro or di-chlorophosphonium chlorides 6 or 7. The divinyl telluride 8 is then produced by the Wittig reaction of 5 with the aldehyde (Scheme 1).

Our efforts to isolate the chlorinated phosphonium salts 6 or 7 as pure compounds were unsuccessful due to the intractable nature of these materials.

The reactions with aromatic aldehydes were not stereoselective under the conditions employed, giving Z,Z, E,Z and E,E isomer mixtures, with a preferential E geometry (from the E,Z and E,E isomers). This fact can be easily deduced from the ¹H-NMR spectra of the reaction with benzaldehyde where a 16.6 Hz coupling constant of the doublets at δ 7.12 and 7.13 ppm (H α to Te) and 7.44 and 7.48 ppm (for H β to Te) was observed. The formation of E geometry on the double bonds is also confirmed by treatment with *n*-BuLi and capture of the intermediate vinyllithium with benzaldehyde [6b]. The allylic alcohol was isolated with 50% yield in a ca. 4:1 ratio as assessed by ¹H-NMR (*E:Z*).





Scheme 2.

By performing the olefination reaction in the presence of 30% HMPA as a co-solvent, the Z,Z isomer becomes predominant (doublets at δ 7.00 and 7.43 ppm with J = 10.6 Hz) as deduced from ¹H-NMR (200 MHz) and by comparison with an authentic sample prepared by another route [6b]. The predominant formation of Z geometry was confirmed by treatment with *n*-BuLi followed by benzaldehyde giving the corresponding allylic alcohol, PhCH=CHCH(OH)Ph, in 64% yield (see Section 3.2) and in a 1:5 ratio as assessed by ¹H-NMR (E:Z).

In the case of aliphatic aldehydes, the Z geometry (from the Z,Z and Z,E isomers) is preferred in both solvent systems, as can be deduced from the ¹H-NMR (400 MHz). For example, ¹H-NMR of the reaction product with isobutyraldehyde shows a doublet of doublets at δ 6.06 ppm (J = 9.2 and 8.8 Hz) and two doublets at 6.40 (J = 8.8 Hz) and 6.43 ppm (J = 9.2Hz). With *n*-butyraldehyde and using HMPA as co-solvent, the Z geometry is also predominant (¹H-NMR, 400 MHz, a doublet at δ 6.55 ppm, H α to Te, J = 9.2Hz). A small doublet at δ 6.51 ppm (J = 16.0 Hz; H α to Te) can be identified for the *E*-isomer.

A metal salt and base dependence was observed both on the stereochemistry of the divinyl tellurides as well as on the yield (for the reaction with benzaldehyde). Using KH instead of *n*-BuLi in THF, the Z,Z-product was formed almost exclusively, but in only 12% isolated yield. Other bases like LDA and LiN(SiMe₃)₂ also gave the products in very low yield.

An alternative methodology was also studied. The starting bis-tellurophosphorane **5** was prepared in situ by means of a transylidation reaction between TeCl_4 and an excess of alkylidenetriphenylphosphorane (generated from the corresponding phosphonium salt and *n*-BuLi) **9**. The tellurobisphosphorane **5** reacted with aldehydes giving the expected divinyl tellurides **8** in acceptable yields (Scheme 2). Again, inversion of the stereochemistry was observed by the use of HMPA as a co-solvent. The yields obtained by both methods are in the same range. The reactions were also performed on a larger scale (3 or 5 mmol, see Table 1) with comparable yields.

To illustrate the usefulness of the prepared compounds, we performed the transmetalation of bis-vinyl tellurides with *n*-BuLi at -78° C, which can be employed to prepare α,β -unsaturated aldehydes 10 by treatment of the intermediate vinyllithiums with DMF

46 Table 1

Diviny	l tellurides	prepared fr	om the tellu	rophosphonium	n salt 1 (Scher	ne 1) an	d from Te	Cl ₄ (Scheme)	2)
		preparea m	0111 0110 00110	ropnoopnomum				Cig (Seneme)	-,

Product	R	Yield (%) from T	e-salt 1	Yield (%) from TeCl ₄		
		THF	THF/HMPA	THF	THF/HMPA	
8a	C ₆ H ₅	44 (33 ^a)	43 (43 ^a)	48 (45 ^b)	30	
8b	$4 - MeC_6H_4$	47	25	46	28	
8c	2-Furyl	30	24	42	42	
8d	$4-ClC_6H_4$	45	27	20	30	
8e	(CH ₃) ₂ CH	20	45	34	15	
8f	CH ₃ CH ₂ CH ₂	22	27	25	34	

^a Reaction performed on 3 mmol scale.

^b Reaction performed on 5 mmol scale.

(Scheme 3). These aldehydes, irrespective of the geometry of the starting bis-vinyl telluride, were formed with *E*-stereochemistry under the conditions employed (DMF added at -78° C, followed by stirring at room temperature for 2 h). For reactions performed only at -78° C, an isomeric mixture of *E*:*Z* isomers **10b** is isolated (8:1 ratio, for Ar = 4-MeC₆H₄), in essentially the same yield.

Considering that the described reaction is feasible for both aromatic and aliphatic aldehydes, thus providing dialkyl vinylic tellurides which can hardly be obtained by hydrotelluration of alkyl acetylenes, and that the yields, in spite of being moderate, are obtained under simple experimental conditions and are not far from the theoretical, the described method is certainly a useful contribution for the preparation of symmetrical divinyl tellurides.

3. Experimental

3.1. General

¹H- and ¹³C-NMR spectra of CDCl₃ solutions were recorded on a 200 MHz (Bruker DPX 200), or a 400 MHz (Bruker DPX 400) spectrometer as noted. Chemical shifts are expressed as parts per million (ppm) with respect to tetramethylsilane as an internal standard. Mass spectra (EI) were obtained at 70 eV with a Hewlett–Packard EM/CG HP-5988A spectrometer. Elemental analyses were performed on a Vario EL Elementar Analysensysteme. Reactions were conducted in oven-dried (120°C) glassware under a nitrogen atmosphere. Merck silica gel (230–400 mesh) was used for flash chromatography. THF was distilled over sodium/ benzophenone immediately before use.

3.2. Synthesis of symmetrical divinyl tellurides. Typical procedures

3.2.1. Preparation of **8a** from tellurophosphonium salt **1** To a solution of tellurophosphonium salt **1** (0.539 g, 0.5 mmol) in dry THF (5 ml) at -78° C under nitrogen, a solution of LICA-lithium dicyclohexylamide (3 mmol) in THF (3 ml) was added dropwise. After 3 h of stirring at this temperature, benzaldehyde (0.159 g, 1.5 mmol) was added. The temperature was raised to room temperature, the mixture was stirred for 2 h and then treated with water and extracted with ethyl acetate $(3 \times 25 \text{ ml})$. The organic layer was dried over MgSO₄ and the solvent removed under vacuum. The residue was purified by column chromatography over silica gel, eluting with hexane, to afford the bis-(2-phenylethenyl)telluride 8a (mixture of isomers). Yield 0.073 g, 44%. ¹H-NMR (200 MHz, CDCl₃, δ ppm) 7.00 (d, 1H, J = 10.6 Hz); 7.09 (d, 1H, J = 10.6 Hz); 7.12 (d, 1H, J = 16.6 Hz); 7.13 (d, 1H, J = 16.6 Hz); 7.20–7.38 (m, 10H); 7.43 (d, 1H, J = 10.6Hz); 7.44 (d, 1H, J = 16.6 Hz); 7.48 (d, 1H, J = 16.6 Hz); 7.49 (d, 1H, J = 10.6 Hz); Anal. Calcd for $C_{16}H_{14}Te$ (333.88): C, 57.56; H, 4.23. Found: C, 57.28; H, 4.19. MS (m/z): 337 [M⁺ + 1], 256, 167 (100%), 77.

3.2.2. Preparation of 8e by $TeCl_4$ method

To a solution of methyltriphenylphosphonium iodide (2.43 g, 6 mmol) in dry THF (25 ml) under nitrogen, at room temperature, *n*-BuLi (6 mmol) was added dropwise. After stirring at room temperature for 20 min the solution was cooled to -78° C and a solution of TeCl₄ (0.270 g, 1 mmol) in dry THF (10 ml) was added. The mixture was stirred for 20 min and isobutyraldehyde (0.216 g, 3 mmol) was added. The temperature was raised to room temperature, the mixture was stirred for 3 h and then treated with water and extracted with ethyl acetate (3 × 25 ml). The organic layer was dried over MgSO₄ and the solvent removed under vacuum. The residue was purified by column chromatography over silica gel, eluting with hexane, to afford **8e** (mixture of isomers).



Scheme 3.

Yield 0.09 g, 34%. ¹H-NMR (400 MHz, CDCl₃, δ ppm) 0.95–1.12 (m, 12H); 2.2–2.5 (m, 2H); 6.06 (dd, 1H, J = 9.2 Hz, J = 8.8 Hz); 6.20 (dd, 1H, J = 16.2 Hz, J = 6.6 Hz); 6.21 (dd, 1H, J = 16.2 Hz, J = 6.6 Hz); 6.21 (dd, 1H, J = 16.2 Hz, J = 6.6 Hz); 6.40 (d, 1H, J = 8.8 Hz); 6.43 (d, 1H, J = 9.2 Hz); 6.48 (dd, 1H, J = 16.4 Hz, J = 1.2 Hz); 6.49 (dd, 1H, J = 16.4 Hz, J = 1.2 Hz); 6.49 (dd, 1H, J = 16.4 Hz, J = 1.2 Hz). MS (m/z): 268 [M⁺], 95, 69 (100%), 41.

3.3. (Z,E)-Phenyl-1-hydroxy-3-phenylprop-2-ene from (Z,Z; E,Z and E,E)-bis-(2-phenyl ethenyl) telluride

To a solution of bis(2-phenylethenyl) telluride (0.334g, 1 mmol) in THF (4 ml) at -78° C under nitrogen, a solution of n-BuLi (0.91 ml, 2.2 mmol, 2.42 M solution in hexane) was added dropwise. After 20 min of stirring at this temperature, benzaldehyde (0.265 g, 2.5 mmol) was added. The mixture was stirred for 30 min, then diluted with ethyl acetate (30 ml) and washed with brine $(4 \times 15 \text{ ml})$. The organic layer was separated, dried over MgSO₄ and solvent removed under vacuum. The residue was purified by column chromatography over silica gel. Elution with hexane removed dibutyl telluride, and elution with ethyl acetate gave an oil. Yield 0.269 g, 64%, E:Z = 1:5. ¹H-NMR (200 MHz, CDCl₃, δ ppm) E + Z isomers: 2.59 (s, 1H); 7.10–7.40 (m, 10H). Z isomer: 5.55 (d, 1H, J = 9.2 Hz); 5.85 (dd, 1H, J = 11.4, 9.2 Hz); 6.59 (d, 1H, J = 11.4 Hz). E isomer: 5.25 (d, 1H, J = 6.2 Hz); 6.29 (dd, 1H, J = 15.8Hz, J = 6.2 Hz); 6.59 (d, 1H, J = 15.8 Hz).

3.4. (E)-p-Methylcynnamaldehyde **10b** from (Z,Z; E,Z and E,E)-bis-[2(p-tolyl)ethenyl] telluride

To a solution of bis-[2-(p-tolyl) ethenyl] telluride (0.362 g, 1 mmol) in THF (4 ml) at -78°C under nitrogen, a solution of n-BuLi (0.91 ml, 2.2 mmol, 2.42 M solution in hexane) was added dropwise. After 20 min of stirring at this temperature, DMF (0.2 ml, 2.58 mmol) was added. The temperature was raised to room temperature and stirred for 2 h, then diluted with ethyl acetate (30 ml), and washed with water (3 × 20 ml). The organic layer was separated, dried with MgSO₄ and solvent removed under vacuum. Elution with hexane removed dibutyl telluride, and elution with ethyl acetate gave a low m.p. solid, 0.175 g, 60% (characterized as the semicarbazone: m.p. 208.4–209.4°C; Literature [11] 210°C). ¹H-NMR (200 MHz, CDCl₃, δ ppm) 2.37 (s, 3H); 6.65 (dd, 1H, J = 15.9, 7.6 Hz); 7.21 (d, 2H, J = 8.0 Hz); 7.37–7.46 (m, 3H); 9.65 (d, 1H, J = 7.6 Hz).

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References

- For recent reviews on the application of tellurium reagents in organic synthesis see: (a) N. Petragnani, J.V. Comasseto, Synthesis (1986) 1; (1991) 793 and 897. (b) N. Petragnani, Best Synthetic Methods—Tellurium in Organic Synthesis, Academic Press, New York, 1994. (c) I.D. Sadekov, V.I. Minkin, Russ. Chem. Rev. 64 (1995) 491. (d) N. Petragnani, in: McKillop (ed.), Comprehensive Organometallic Chemistry II, vol. 11, 1995, Chap. 14, 571. (e) N. Petragnani, W.L. Lo, Phosphorus Sulphur Silicon 136–138 (1998) 91.
- [2] (a) N.K. Gusarova, A.A. Takarinova, M. Sirregovskaya, Sulfur Reports 11 (1991) 1. (b) J.V. Comasseto, in: S. Oae (ed.), Reviews in Heteroatom Chemistry, vol. 9, MYU, Tokyo, 1993, p. 61.
- [3] J.V. Comasseto, W.L. Lo, N. Petragnani, H.A. Stefani, Synthesis (1997) 373.
- [4] Ref. [3], Section 3.2.2.
- [5] (a) Ref. [3], Section 3.3. (b) F.C. Tucci, A. Chieffi, J.V. Comasseto, J.P. Marino, J. Org. Chem. 61 (1996) 4975.
- [6] (a) H. Takahashi, K. Ohe, S. Uemura, N. Sugita, Nippon Kagaku Kaishi (1987) 1508. (b) S.M. Barros, M.J. Dabdoub, V.M. Dabdoub, J.V. Comasseto, Organometallics 8 (1989) 1661.
- [7] C.C. Silveira, G. Perin, A.L. Braga, N. Petragnani, Synlett (1995) 58.
- [8] (a) A very stable colored salt prepared by the reaction of TeCl₄ with two equivalents of Ph₃PCH₃]⁺I⁻. (b) N. Petragnani, L. Torres, J. Organomet. Chem. 76 (1974) 241.
- [9] The yield was not increased by treatment of the crude of reaction mixture with $NaBH_4$ to reduce any divinyl tellurium dichloride to **8**.
- [10] (a) D.B. Densey, S.T. Ross, J. Org. Chem. 26 (1962) 99. (b) A.N. Pudovik, I.M. Aladzheva, L.N. Yakovenko, Zh. Obsch. Khim. 35 (1965) 1210 [C.A., 63 (1965) 11609]. (c) A.J. Speziale, K.W. Rath, J. Org. Chem. 28 (1963) 465. (d) E. Zbiral, M. Rasberger, Tetrahedron 25 (1969) 1871. (e) R. Amos, J. Org. Chem. 50 (1985) 1311. (f) X.Y. Li, Y.S. Hu, Tetrahedron Lett. 28 (1987) 6317. (g) K. Yamagata, M. Takaki, M. Yamazaki, Liebigs Ann. Chem. (1993) 1109.
- [11] M. Scholtz, A. Wiedemann, Ber. Dtsch. Chem. Ges. 36 (1903) 845.