Stereoselective synthesis of ketene telluroacetals *via* hydrozirconation of acetylenic tellurides

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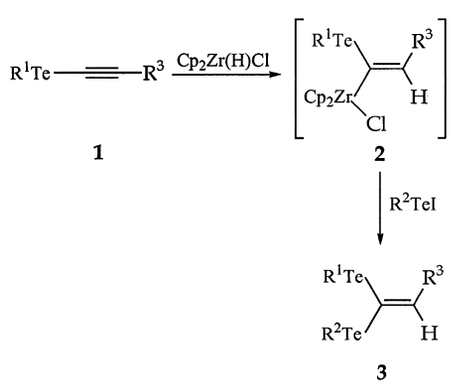
1 PERKIN COMMUNICATION

Hydrozirconation of acetylenic tellurides 1 gives organozirconium(IV) complexes 2, which are trapped with tellurenyl iodides to afford ketene telluroacetals 3.

Organotelluro compounds play an important role in organic synthesis. From the several classes of organotelluro compounds, vinylic tellurides are of particular interest, mainly as precursors of vinyllithium and vinylcopper reagents *via* transmetallation.[1] Although ketene telluroacetals could be very useful as 1,1-dilithioethene equivalents,[2] to our knowledge only two methods have been described for their preparation, involving the insertion of a vinylic carbene into the Te–Te bond of a ditelluride (two examples in low yield),[3] and reaction of methylphosphonate or phenyltelluromethylphosphonate with base and PhTeBr and subsequently with aldehydes (seven examples in good to excellent yield).[4]

In a previous paper, we reported the stereo- and regioselective preparation of vinyl tellurides *via* alkenyl zirconocenes,[5] and the hydrozirconation of acetylenic tellurides.[6] As an extension of our studies, we are interested in developing new synthetic routes toward ketene telluroacetals. We describe here a stereoselective preparation of ketene telluroacetals **3**, by the hydrozirconation of acetylenic tellurides **1** and then transmetallation using tellurenyl iodides (Scheme 1).



Scheme 1

Acetylenic tellurides **1** were synthesized in high yield according to the method of Dabdoub and Comasseto.[7] Hydrozirconation of acetylenic tellurides **1** is found to proceed stereoselectively in *cis* fashion with high regioselectivity affording 1,1-bimetalloalkenes of tellurium and zirconium **2**.[6] The intermediates **2** are converted to ketene telluroacetals **3** after treatment with alkyltellurenyl iodide (Table 1). The intermediates **2** are cleaved with essentially complete retention of configuration by alkyltellurenyl iodide[5] to give stereodefined ketene telluroacetals **3**, which are difficult to prepare by other means.[3,4] The mass spectra are very characteristic due to the large number of isotopes of tellurium (isotopic abundance: ^{130}Te 33.8%, ^{128}Te 31.7%, ^{126}Te 19.0%, ^{125}Te 7.1%, ^{124}Te 4.8%). In all cases, the calculated molecular ion isotope pattern matches well with the experimental isotope pattern. Although products **3** are isolable and easily handled, they decompose in solution to an insoluble white powder and other compounds in a matter of days.[3] Butyl telluroacetal **3b** is less stable than phenyl telluroacetal **3c**. Butyl phenyl telluroacetals, **3a**, **3d** and **3e**, decompose in a more complicated way than **3b** and **3c**.

Table 1 Preparation of ketene telluroacetals **3a**–**3e**

Entry	R^1	R^2	R^3	Product	Yield (%)[a]
1	Bu	Ph	Bu	**3a**	70
2	Bu	Bu	Bu	**3b**	65
3	Ph	Ph	Bu	**3c**	62
4	Ph	Bu	Bu	**3d**	57
5	Bu	Ph	$(CH_2)_3OBn$	**3e**	60

[a] Isolated yield.

Our methodology is quite efficient for several reasons: (i) the mild nature of the conditions involved; (ii) the excellent regio- and stereo-chemical control of hydrozirconation; (iii) the one-pot nature of the procedure.

Experimental

^{1}H NMR and ^{13}C NMR spectra were obtained on a Bruker AM-200 spectrometer with tetramethylsilane as internal standard in $CDCl_3$; *J* values are given in Hz. Mass spectra were obtained on a Hewlett Packard 5985A GC–MS system using the electron impact method.

General procedure for the stereoselective synthesis of ketene telluroacetals 3a–3e

A slurry was prepared from $Cp_2Zr(H)Cl$ (1.1 mmol) and 5 ml of THF at room temperature under a nitrogen atmosphere, and the acetylenic telluride **1** (1 mmol) in 2 ml of THF was added *via* a syringe. The mixture was stirred at room temperature for 10–25 min, until hydrozirconation was complete, as evidenced by the disappearance of the insoluble hydride and the formation of a clear solution. To this solution, which contained the intermediate **2**, was added 1.1 equiv. of alkyltellurenyl iodide (prepared *in situ* by the addition of iodine solution to a stirred solution of dialkyl ditelluride)[8] at room temperature. After stirring for 1 h, normal work-up was performed. Ketene telluroacetal **3** was isolated and purified by column chromatography using hexane as eluent.

Compound 3a. δ_H 7.74–7.69 (m, 2 H), 7.26–7.20 (m, 3 H), 6.70 (t, *J* 6.9, 1 H), 2.74 (t, *J* 7.5, 2 H), 2.24–2.16 (m, 2 H), 1.72–1.60 (m, 2 H), 1.41–1.24 (m, 6 H), 0.91–0.82 (m, 6 H); δ_C 155.74, 137.50, 129.42, 127.75, 117.93, 77.80, 39.00, 33.94, 30.89, 25.16, 22.26, 13.94, 13.64, 13.45; *m/z* 476 (M^+, 3.5%, ^{130}Te^{130}Te), 474 (M^+, 6.0%, ^{130}Te^{128}Te), 472 (M^+, 7.1%, ^{130}Te^{126}Te, ^{128}Te^{128}Te), 470 (M^+, 4.6%, ^{130}Te^{124}Te, ^{128}Te^{126}Te).

Compound 3b. δ_H 6.68 (t, *J* 6.9, 1 H), 2.74 (t, *J* 7.4, 4 H), 2.21 (q, *J* 6.9, 2 H), 1.81–1.66 (m, 4 H), 1.42–1.28 (m, 9 H); δ_C 154.47, 75.73, 39.05, 33.83, 33.32, 30.96, 25.13, 22.16, 13.90,

13.61, 13.45, 13.34, 11.74; *m/z* 456 (M^+, 4.5%, $^{130}Te^{130}Te$), 454 (M^+, 5.6%, $^{130}Te^{128}Te$), 452 (M^+, 6.5%, $^{130}Te^{126}Te$, $^{128}Te^{128}Te$), 450 (M^+, 4.6%, $^{130}Te^{124}Te$, $^{128}Te^{126}Te$).

Compound 3c. δ_H 7.74–7.68 (m, 4 H), 7.36–7.17 (m, 6 H), 6.65 (t, *J* 6.9, 1 H), 2.26 (q, *J* 7.0, 2 H), 1.41–1.29 (m, 4 H), 0.90 (t, *J* 6.8, 3 H); δ_C 153.25, 138.59, 138.56, 129.26, 129.04, 127.94, 127.89, 117.96, 116.49, 79.96, 38.90, 30.74, 22.13, 13.87; *m/z* 496 (M^+, 5.2%, $^{130}Te^{130}Te$), 494 (M^+, 7.2%, $^{130}Te^{128}Te$), 492 (M^+, 7.5%, $^{130}Te^{126}Te$, $^{128}Te^{128}Te$), 490 (M^+, 5.3%, $^{130}Te^{124}Te$, $^{128}Te^{126}Te$).

Compound 3d. δ_H 7.77–7.72 (m, 2 H), 7.28–7.22 (m, 3 H), 6.74 (t, *J* 6.9, 1 H), 2.77 (t, *J* 7.5, 2 H), 2.28–2.21 (m, 2 H), 1.75–1.64 (m, 2 H), 1.45–1.33 (m, 6 H), 0.95–0.85 (m, 6 H); δ_C 155.44, 138.00, 137.35, 129.27, 129.07, 127.58, 117.89, 77.96, 38.88, 33.84, 30.79, 25.06, 22.15, 13.884, 13.585, 13.397; *m/z* 476 (M^+, 3.8%, $^{130}Te^{130}Te$), 474 (M^+, 6.3%, $^{130}Te^{128}Te$), 472 (M^+, 7.1%, $^{130}Te^{126}Te$, $^{128}Te^{128}Te$), 470 (M^+, 4.6%, $^{130}Te^{124}Te$, $^{128}Te^{126}Te$).

Compound 3e. δ_H 7.78–7.74 (m, 2 H), 7.40–7.23 (m, 8 H), 6.73 (t, *J* 6.9, 1 H), 4.50 (s, 2 H), 3.48 (t, *J* 6.4, 2 H), 2.78 (t, *J* 7.4, 2 H), 2.37 (q, *J* 7.2, 2 H), 1.80–1.69 (m, 4 H), 1.41–1.30 (m, 2 H), 0.90 (t, *J* 7.3, 3 H); δ_C 154.05, 138.35, 137.54, 129.34, 128.23, 127.69, 127.44, 117.82, 111.54, 78.64, 72.78, 69.37, 35.86, 33.84, 28.71, 25.05, 13.57, 13.40.

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