First synthesis and characterization of vinylselenols and vinyltellurols

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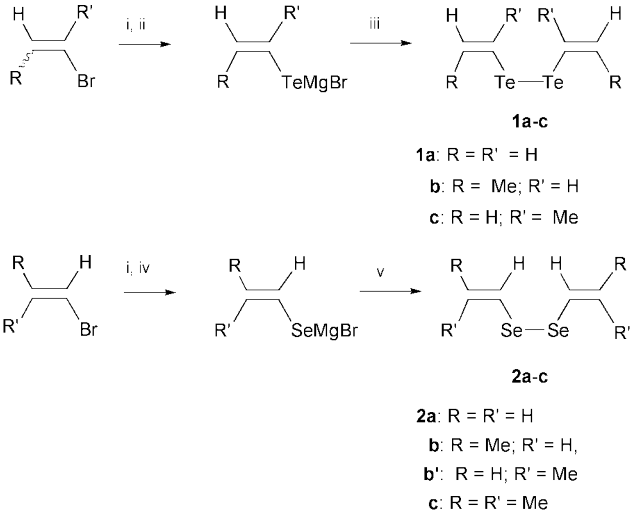
Vinylselenols and vinyltellurols have been prepared by slow addition of tributyltin hydride to the corresponding divinyldiselenide or divinylditelluride in tetraglyme.

Several α,β-unsaturated heterocompounds bearing one or several hydrogen atom(s) on the heteroatom exhibit interesting properties. For instance, base-induced keto–enol or imine–enamine tautomerism is a consequence of the high acidity of the hydrogen linked to the heteroatom.[1] Recently, evidence for a similar increase of acidity between saturated and α,β-unsaturated phosphines and arsines was provided by FT-ICR mass spectrometry and theoretical calculations.[2] From a synthetic viewpoint, the rearrangement of such α,β-unsaturated compounds provides an efficient method for the preparation or the chemical trapping of the corresponding carbon–heteroatom multiple bond derivatives.[3] Although primary α,β-unsaturated derivatives of mercury, silicon, germanium, tin, nitrogen, phosphorus, arsenic, antimony, oxygen and sulfur have been reported,[4] no primary α,β-unsaturated selenol or tellurol derivatives have been isolated so far.[5] Such compounds, which are probably unstable in a variety of experimental conditions, cannot be easily prepared by conventional approaches used for other heterocompounds.

Flash vacuum pyrolysis is an efficient technique to prepare derivatives of the elements of the first and second rows of the periodic table and vinylthiols have also been prepared by this method.[6] However, with the elements of subsequent rows, the energy of the carbon–heteroatom bond is often too low to withstand high temperatures. The preparation of thiols, selenols or tellurols *via* LAH or other reducing agents such as borohydrides requires an acidolysis of the resulting salt to isolate the free product.[7] Although quite stable compounds such as vinylthiols have been prepared in this manner,[8] such approaches are not viable for sensitive α,β-unsaturated derivatives of selenols and tellurols.

Since 1994, we have been involved in the synthesis of primary low boiling α,β- or β,γ-unsaturated phosphines, arsines, stibines, stannanes and mercury hydrides.[3,9–12] We have developed an efficient procedure for the preparation of these compounds using vacuum line techniques, *via* the reduction of the corresponding halo derivatives with excess tributyltin hydride. This approach cannot be used to prepare SH, SeH or TeH derivatives because these products would quickly react with the tin hydride to form the corresponding S–Sn, Se–Sn or Te–Sn derivatives. However, Crich *et al.* have recently shown that a selenol (PhSeH) can be detected for a short time by addition of Bu_3SnH to a solution of diphenyldiselenide.[13] By combining this approach with the experimental technique developed in our laboratory, we looked into the preparation of kinetically unstable selenols and tellurols. We now report here, the synthesis of low boiling vinylselenols and tellurols starting from the corresponding divinyldiselenides or ditellurides.

The synthesis of divinylditellurides has been reported by Dabdoub and Comasseto.[14] The arial oxidation of the product formed by insertion of tellurium in vinyl Grignard reagents led to compounds **1a–c** (Scheme 1). Starting from a mixture of *Z*- and *E*-isomers of 1-bromopropene, only the *Z*-dipropenylditelluride **1b** was obtained. The simple divinyldiselenides have never been reported before. We prepared the divinyldiselenides **2a–c** starting from selenium and vinyl Grignard reagents using dibromine as the oxidizing reagent (yields: 52–73%). Compounds **2a–c** have been unambiguously characterized by ^1H, ^{13}C, ^{77}Se NMR and high resolution mass spectrometry (HRMS). The ^{77}Se NMR signals were observed between δ 236 (**1c**) and δ 407 (**1b′**).[15]



1a-c

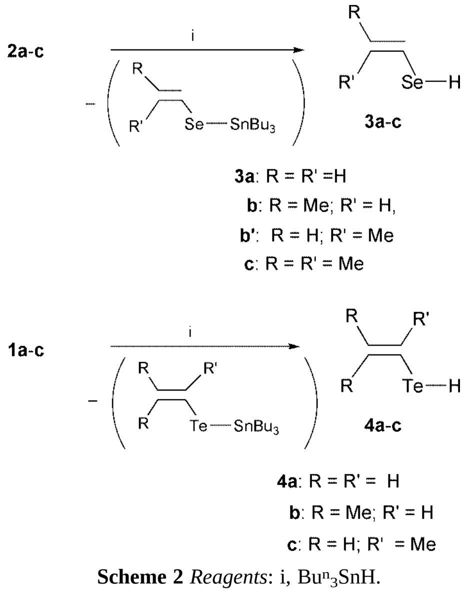
1a: R = R' = H
b: R = Me; R' = H
c: R = H; R' = Me

2a-c

2a: R = R' = H
b: R = Me; R' = H,
b': R = H; R' = Me
c: R = R' = Me

Scheme 1 *Reagents and conditions*: i, Mg; ii, Te, reflux, 30 min; iii, air; iv, Se, room temp.; v, Br_2, −20 °C.

The vinylselenols **3a–c** and vinyltellurols **4a–c** were prepared by slow addition of 1.5 equiv. of Bu_3SnH to a solution of **2a–c** or **1a–c**, respectively, in tetraglyme (Scheme 2).† The products were continuously distilled *in vacuo* from the reaction mixture and condensed in a cold trap. They were thus isolated before their reaction with the tin hydride. Vinylselenols **3a–c** were obtained in good yields (73–83%) but only moderate yields



3a-c

3a: R = R' =H
b: R = Me; R' = H,
b': R = H; R' = Me
c: R = R' = Me

4a-c

4a: R = R' = H
b: R = Me; R' = H
c: R = H; R' = Me

Scheme 2 *Reagents*: i, Bu^n_3SnH.

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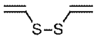
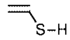
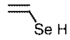
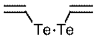
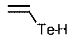
Table 1 Yield and selected NMR data for the ethyl and ethenyl selenium and tellurium derivatives

	Yield^a (%) (lit.)	δ_H X-H	XCH	$^1J_{X\text{-}H}$	δ_C $\delta_{C\alpha}$	$\delta_{C\beta}$	δ_X
EtSH	96	1.39	2.53	-	19.5	18.9	-
EtSeH	89 (86)^b	-0.56	2.62	47.5	12.1	20.1	29^c
EtTeH	83 ()^{d,e}	-4.68	2.65	45.7	-9.7	21.1	-44.7
 S–S	(50-70)^f	-	6.25	-	131.4	114.4	-
 S–H	87 (≈60)^g	2.97	6.30	-	123.9	115.7	-
 Se-Se	63 (crude)	-	6.69	-	119.7	124.9	388.8
 Se H	73	1.06	6.61	59.8	118.4	120.5	113.6
 Te-Te	(67)^h	-	7.13	-	101.8	131.3	282.9
 Te-H	32	-2.97	6.93	25.6	100.0	130.5	70.4

^{a} This work. ^{b} Ref. 16. ^{c} Ref. 15. ^{d} Yield not given, ref. 17. ^{e} Ref. 18. ^{f} Ref. 19. ^{g} Ref. 8. ^{h} Ref. 14.

(32–43%) were observed for the more reactive tellurols **4a–c**.‡

All compounds **3a–c**, **4a–c** were unambiguously characterized by ^{1}H, ^{13}C, ^{77}Se or ^{125}Te NMR spectroscopy and HRMS.§ In the ^{1}H NMR spectrum, the presence of an unsaturated group on a heteroatom usually leads to a downfield shift of the signals of hydrogen(s) attached to the heteroatom and an increase in the coupling constants.[9,11] In the ^{1}H NMR spectra of selenols **3a–c**, the signal of the hydrogen on the selenium atom was observed *ca.* 1.5 ppm downfield to that of the saturated derivative (Table 1). A similar downfield effect was observed for the tellurols. The $^1J_{SeH}$ and $^1J_{SeC}$ coupling constants of the unsaturated compounds **3a–c** are higher than those of the saturated compounds [$^1J_{SeC}$ (**3a**): 93.2 Hz, $^1J_{SeC}$ (EtSeH): 45.0 Hz]. This can be attributed to an increase of the s character of the Se–H and Se–C bonds. Although a similar increase was observed for the $^1J_{TeC}$ coupling constant of tellurols [$^1J_{TeC}$ (**4a**): 247.3 Hz, $^1J_{TeC}$ (EtTeH): 114.9 Hz], an opposite effect was observed for the $^1J_{TeH}$ coupling constants. To the best of our knowledge although a upfield signal has been observed for the proton on the mercury atom of the vinyl derivative,[12] such a decrease of a $^1J_{XH}$ coupling constant for a vinylic derivative has never been reported.

Vinylselenols and vinyltellurols exhibit a low stability at room temperature: the half-life of selenols **3a–c** diluted in $CDCl_3$ is *ca.* one day and *ca.* 60 min for the tellurols **4a–c**. Only insoluble black decomposition products were observed after a few days.

In conclusion, we have successfully prepared vinylselenols and tellurols by reaction of Bu_3SnH with the corresponding diselenide or ditelluride derivatives. By reaction with a hydride ($Bu^n{}_3SnH$), compounds bearing an acidic hydrogen (RSH, RSeH, RTeH) were prepared *via* a radical reaction thus providing a new route which is an alternative to the hydrolytic method. Further investigation into the synthesis of other unsaturated selenols and tellurols, and spectroscopic studies are currently under progress in our lab.

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Notes and references

† *Typical experimental procedure*: (**CAUTION:** *Selenols and tellurols are potentially highly toxic compounds and must be used with great care under a well-ventilated hood*). The apparatus already described for the reduction of dichlorostibines was used.[10] The flask containing the precursor [2 mmol of **1a–c** or **2a–c** diluted in tetraglyme (5 mL)] was fitted on a vacuum line and degassed. $Bu^n{}_3SnH$ (3 mmol) was then slowly added (30 min) at room temperature with a syringe through the septum. During and after the addition, vinylselenols **3a–c** or tellurols **4a–c** was distilled off *in vacuo* (10^{-1} mbar) from the reaction mixture. A cold trap (−60 °C) removed selectively the less volatile products and compounds **3a–c**, **4a–c** were condensed on a cold finger (−196 °C) connected at the bottom to a flask or an NMR tube. A co-solvent can be added at this step. After disconnecting from the vacuum line by stopcocks, the apparatus was filled with dry nitrogen; liquid nitrogen was subsequently removed. The product was collected in a Schlenk flask or a NMR tube and kept at low temperature (< −50 °C) before analysis.

‡ Under these experimental conditions, we have also prepared alkylthiols (EtSH, yield: 96%), vinylthiols (MeCH=CHSH, yield: 91%), arylthiols (PhSH, yield: 77%), alkylselenols (EtSeH, yield: 89%) and alkyltellurols (EtTeH, yield: 83%). The reaction with EtSeSEt led to ethanethiol (yield: 92%) and traces of EtSeH suggesting that the ethylseleno group acts as a protecting group for the thiol.

§ *Selected data:* **3b,b′**: bp (0.1 Torr) ≈ −70 °C. Yield: 83%. $\tau_{1/2}$ (5% in $CDCl_3$) ≈ 25 h. (*E*)-**3b**: δ_H(400 MHz, $CDCl_3$, −40 °C) 0.78 [d, 1H, *J* 5.3, $^1J_{SeH}$ 60.7 Hz (d), SeH], 1.72 (d, 3H, *J* 6.4 Hz, CH_3), 5.98 (dq, 1H, *J* 15.3, 6.4 Hz, CH), 6.10 (m, 1H, CH). δ_C(100 MHz, $CDCl_3$, −40 °C) 20.2, 107.4, 133.7. δ_{Se}(57.2 MHz, $CDCl_3$, −40 °C) 31.0. (*Z*)-**3b′**. δ_H(400 MHz, $CDCl_3$, −40 °C) 0.69 (d, 1H, *J* 6.9 Hz, SeH), 1.67 (d, 3H, *J* 6.6 Hz, CH_3); 6.04 (dq, 1H, *J* 8.7, 6.6 Hz, CH), 6.31 (dd, 1H, *J* 8.7, 6.9 Hz, CH). δ_C(100 MHz, $CDCl_3$, −40 °C) 16.0, 110.6, 128.4. δ_{Se} (57.2 MHz, $CDCl_3$, −40 °C) 75.4. HRMS: calc. for $(C_3H_6{}^{80}Se\cdot)^+$ (*Z* + *E*): *m*/*z* 121.9634; found: 121.963. **3c**: bp (0.1 Torr) ≈ −60 °C. Yield: 77%. $\tau_{1/2}$ (5% in $CDCl_3$) ≈ 20 h. δ_H(400 MHz, $CDCl_3$, −40 °C) 0.61 [d, 1H, *J* 5.9, $^1J_{SeH}$ 60.5 Hz (d), SeH]; 1.72 (s, 3H, CH_3), 1.80 (s, 3H, CH_3), 5.95 (d, 1H, *J* 5.9 Hz, CH). δ_C(100 MHz, $CDCl_3$, −40 °C) 20.9, 26.0, 101.8, 138.3. δ_{Se}(57.2 MHz, $CDCl_3$, −40 °C) 26.0. HRMS calc. for $(C_4H_8{}^{80}Se\cdot)^+$: *m*/*z* 135.9791; found: 135.979. **4b**: bp (0.1 Torr) ≈ −50 °C. Yield: 43%. $\tau_{1/2}$ (5% in $CDCl_3$): 1 h. δ_H (400 MHz, $CDCl_3$, −40 °C) −3.43 [d, 1H, *J* 5.4, $^1J_{TeH}$ 26.2 Hz (d), TeH], 1.71 (d, 3H, *J* 6.3 Hz, CH_3), 6.33 (dq, 1H, *J* 9.0, 6.3 Hz, CH), 6.61 (dd, 1H, *J* 9.0, 5.4 Hz, CH). δ_C (100 MHz, $CDCl_3$, −40 °C) 20.6, 94.5, 136.0. δ_{Te}(94.7 MHz, $CDCl_3$, −40 °C) −95.4. HRMS: calc. for $(C_3H_5{}^{130}Te.)^+$: *m*/*z* 171.9539; found: 171.953. **4c**: bp (0.1 Torr) ≈ −50 °C. Yield: 34%. $\tau_{1/2}$ (5% in $CDCl_3$): 1 h. δ_H (400 MHz, $CDCl_3$, −40 °C) −2.78 [s, 1H, $^1J_{TeH}$ 28.5 Hz (d), TeH], 2.34 (t, 3H, *J* 1.3 Hz, CH_3); 5.40 (q, 1H, *J* 1.3 Hz, HC*H*); 5.75 (q, 1H, *J* 1.3, *H*CH). δ_C(100 MHz, $CDCl_3$, −40 °C) 34.1, 116.3, 125.6. δ_{Te} (94.7 MHz, $CDCl_3$, −40 °C) 182.5. HRMS: calc. for $(C_3H_6{}^{128}Te\cdot)^+$: *m*/*z* 171.9539; found: 171.954.

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