Pergamon

Tetrahedron Letters 43 (2002) 1625–1628

TETRAHEDRON
LETTERS

β-Functionalized selenides and tellurides by hydrochalcogenation of olefins containing electron-withdrawing groups

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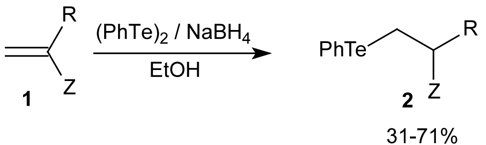
Received 5 December 2001; revised 10 January 2002; accepted 11 January 2002

Abstract—Olefins conjugated to electron-withdrawing groups (e.g. CHO, RCO, CO_2R, CN) react rapidly with alkylselenols and tellurols generated in situ to give the corresponding β-chalcogeno aldehydes, ketones, esters and nitriles. β-Telluroketones are transformed into β-telluroketals, which are β-lithiocarbonyl synthons. © 2002 Elsevier Science Ltd. All rights reserved.

The hydrotelluration of alkynes is a widely explored reaction to prepare vinylic tellurides.[1] The hydrotelluration of alkenes, on the contrary received little attention and, to our knowledge, only a brief mention to this reaction was made in the literature.[2] In 1987 Uemura reported the reaction of α,β-unsaturated esters and nitriles **1** with a mixture of diphenylditelluride and sodium borohydride in ethanol to give the corresponding β-phenyltelluroesters and nitriles **2** in 31–71% yield (Scheme 1).

A limitation of this method is the use of reducing conditions, which can affect some functionalities present in the unsaturated substrates. In addition, if dialkylditellurides are used, the bad smell of these compounds is also a limiting factor. Recently we circumvented these problems by generating organotellurols in situ by the reaction of an organolithium with elemental tellurium in THF followed by addition of a proton source such as ethanol or water, and then reacting the in situ formed tellurol with an alkyne.[3]

In this communication we describe the application of this methodology in the hydrotelluration and hydroselenation of olefins containing electron-withdrawing groups.

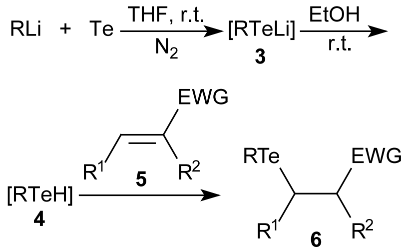


R = H, CH_3; Z = CO_2Et, CN

Scheme 1.

Lithium butyltellurolate (**3**) was prepared by addition of commercial butyllithium to a suspension of elemental tellurium in dry tetrahydrofuran under deoxygenated nitrogen at room temperature. A yellow solution was rapidly formed. To this solution was added 1 equiv. of absolute ethanol and then the olefin containing an electron-withdrawing group (EWG) **5**. After some time TLC analysis showed that all the starting material was consumed. Work-up of the reaction mixture led to the 1,4-addition product **6** in good to excellent yields (Scheme 2, Table 1).[4]

The reaction worked well when mono- and disubstituted olefins were used but failed with trisubstituted ones (entries 7 and 11, Table 1). This methodology failed also when 2,3-cyclohexenone was used. Condensation products of the enone were formed instead of the hydrotelluration product. This problem was solved by using water (2.5 equiv.) instead of ethanol as the proton



R = n-Bu, s-Bu
EWG = CN, CHO, COR, CO_2R

Scheme 2.

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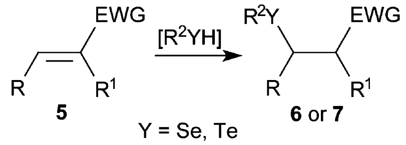
† In memoriam.

PII: S0040-4039(02)00095-3

Table 1.



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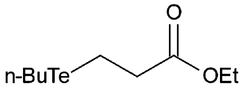
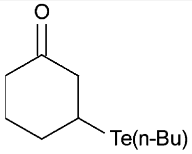
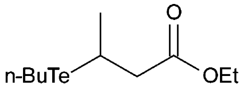
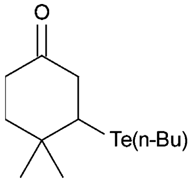
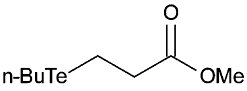
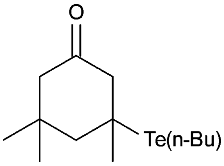
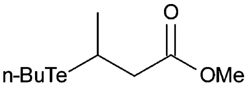
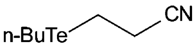
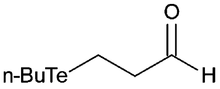
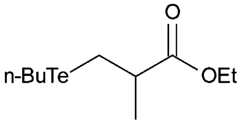
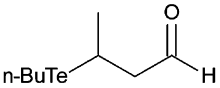
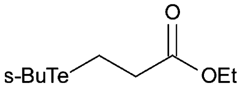
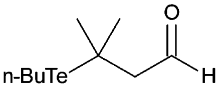
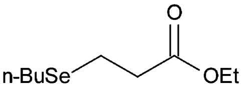
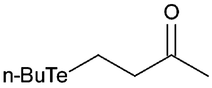
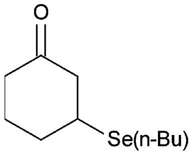
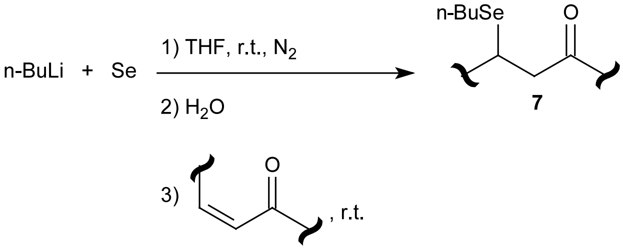
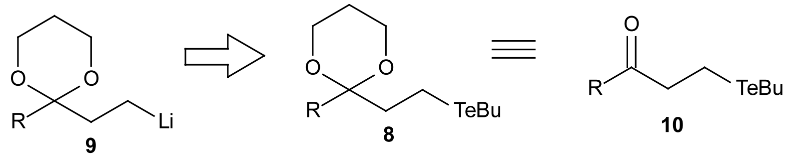
1		96	9		89
3		78	10		62
3		89	11		not formed
4		93	12		98
5		63	13		90
6		56	14		95
7		not formed	15		79
8		86	16		82

source. In this case the hydrotelluration reaction led to the β-butyltellurocyclohexanone in 89% yield (entry 9, Table 1). The use of water as the proton source was successful also for the other olefinic substrates. In this way, it is recommended to use water instead of ethanol to generate the tellurol.

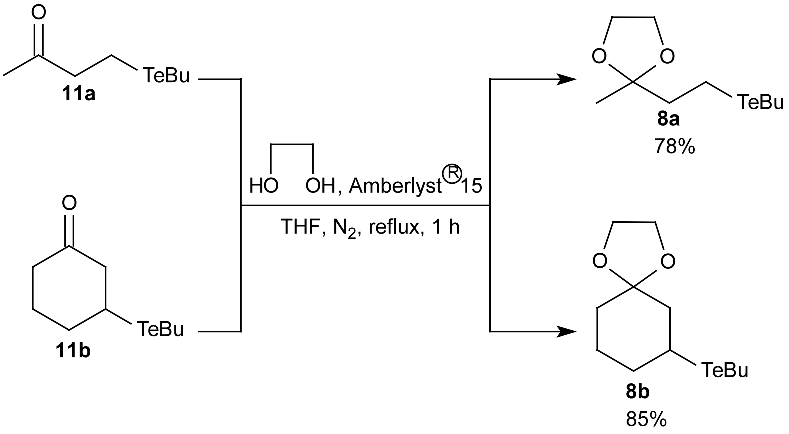
The above described methodology was successfully used to prepare also β-seleno carbonyl compounds **7** in good yields (Scheme 3, entries 15 and 16, Table 1).



Scheme 3.



Scheme 4.



Scheme 5.

This method generates alkylselenols in situ avoiding the isolation of selenols, which are very bad smelling compounds. The most synthetically useful application of organotellurides is their transformation into reactive organometallics, such as organolithium, magnesium, zinc and copper species.[5] Some time ago Sonoda and coworkers reported the transformation of β-telluroketals **8** into β-lithioketals **9** by reaction of **8** with *n*-butyllithium, what transforms these compounds into β-lithiocarbonyl synthons **10**[6] (Scheme 4).

In view of this synthetic application of β-telluroketals **8** we transformed **11** into **8**. The transformation occurs in good yield by reacting the β-telluroketones (entries 8 and 9, Table 1) with ethylene glycol in dry tetrahydrofuran in the presence of Amberlyst® 15[7] (Scheme 5).

In view of the easy access to enones, the reaction sequence described by us is a very convenient method to prepare β-telluroketals **8**.

In conclusion, we developed a practical method to prepare β-functionalized tellurides and selenides. The β-tellurocarbonyl compounds were transformed into β-telluroketals, which are β-lithiocarbonyl synthons.

Acknowledgements

The authors would like to thank CNPq and FAPESP for their support.

References

1. For recent reviews, see: (a) Vieira, M. L.; Zinn, F. K.; Comasseto, J. V. *J. Braz. Chem. Soc.* **2001**, *12*, 586; (b) Comasseto, J. V.; Barrientos-Astigarraga, R. E. *Aldrichim. Acta* **2000**, *33*, 66.
2. Ohe, K.; Takahashi, H.; Uemura, S.; Sugita, N. *Nippon Kagaku Kaishi* **1987**, 1469.
3. (a) Zeni, G.; Formiga, H. B.; Comasseto, J. V. *Tetrahedron Lett.* **2000**, *41*, 1311; (b) An intramolecular version of this reaction was developed by Sachida, who prepared several tellurium heterocycles by this method. For a review, see: Sachida, H. *Rev. Heteroatom. Chem.* **2000**, *22*, 59.
4. *Typical procedure for the hydrotelluration of olefins*: In a two-necked 50 mL flask under nitrogen and magnetic stirring was placed elemental tellurium (0.511 g, 4 mmol) in dry THF (5 mL). To this suspension at room temperature was added *n*-butyllithium (3.08 mL of a 1.3 M solution in hexane, 4 mmol). A yellow solution was formed. To this solution was added 1 equiv. of ethyl alcohol. Then ethyl acrylate (0.44 mL, 4 mmol) was added at 0°C. The mixture was allowed to reach the room temperature and maintained under stirring for 1 h, then it was diluted with ethyl acetate (5 mL). The organic phase was washed with NH_4Cl (3×15 mL) solution and brine (3×15 mL) and then dried with magnesium sulfate and the solvent was evaporated. The residue was purified by silica gel column chromatography eluting with hexane. Yield of 3-butyltellanylpropionic acid ethyl ester (entry 1, Table 1): 0.49 g (96%). ^{1}H NMR (300 MHz, $CDCl_3$, ppm) δ 0.92 (t, $J=7.4$ Hz, 3 H); 1.27 (t, $J=7.1$ Hz, 3 H); 1.38 (sext., $J=7.4$ Hz, 2 H); 1.74 (quint., $J=7.4$ Hz, 2 H); 2.68 (t, $J=7.4$ Hz, 2 H); 2.83 (A_2B_2, $\Delta\nu/J=1.5$ Hz, $J=1.1$ Hz, 4 H); 4.15 (q, $J=7.1$ Hz, 2 H). ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 173.15; 60.65; 37.47; 34.33; 25.09; 14.26; 13.41; 3.32; −5.78. ^{125}Te NMR (157 MHzm $CDCl_3$, ppm, Ph_2Te_2 internal standard): δ 279.19. LRMS *m*/*z* (relative intensity, %): 288 (35); 286 (30, M^+); 231 (28); 229 (26); 186 (29); 184 (28); 57 (94); 55 (100). IR (cm^{-1}): 2958; 2928; 2870; 1735. Anal. calcd: C, 37.82; H, 6.35. Found: C, 37.69; H, 6.35%.
5. For recent reviews, see: Ref. 1.

6. Inoue, T.; Atarashi, Y.; Kambe, N.; Ogawa, A.; Sonoda, N. *Synlett* **1995**, 209.

7. *Typical procedure for the transformation of a β-telluroketone into a β-telluroketal*: In a two-necked 50 mL flask under nitrogen and magnetic stirring was placed butyl-(2)-butanoyl telluride (**11a**, 1 g, 3.9 mmol), Amberlyst® 15 (0.2 g) and ethylene glycol (0.62 g, 10 mmol) in dry THF (15 mL). This mixture was allowed to react under reflux for 1 h and then it was diluted with NH_4Cl (5 mL) and ethyl acetate (5 mL). The organic phase was washed with NH_4Cl (3×15 mL) solution and brine (3×15 mL). The organic phase was dried with magnesium sulfate and the solvent was evaporated. The residue was purified by column chromatography on neutral aluminum oxide eluting with hexane/ethyl acetate (10: 1). Yield of 2-(2-butyltellanylethyl)-2-methyl-[1,3]-dioxolane (**8a**):[6] 0.92 g (3.04 mmol, 78%). ^{1}H NMR (300 MHz, $CDCl_3$, ppm) δ 0.92 (t, $J=7.3$ Hz, 3 H); 1.32 (s, 3 H); 1.38 (sext., $J=7.3$ Hz, 2 H); 1.72 (qt, $J=7.3$ Hz, 2 H); 2.10–2.16 (m, 2 H); 2.60–2.66 (m, 4 H); 3.95 (m, 4 H). ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 110.2; 64.6; 42.1; 34.1; 24.9; 23.4; 13.3; 2.6; −5.6. LRMS m/z (relative intensity, %): 302 (3, M^+); 99 (4); 87 (100); 55 (15); 43 (58). IR (cm^{-1}): 2979; 2958; 2927; 2874; 1457; 1378; 1246; 1212; 944.