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Selectivity between deprotonation and attack on tellurium in the reaction of 1,4-thiatellurins with strongly basic reagents

H.J.M. Schoufs [b], A. Maercker [a] and L. Brandsma [b]

[a] *Institut für Organische Chemie der Universität, Adolf-Reichweinstrasse, W-5900 Siegen (Germany)*
[b] *Department of Preparative Organic Chemistry of the University, Debye Institute, 3584 CH Utrecht (Netherlands)*

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Abstract

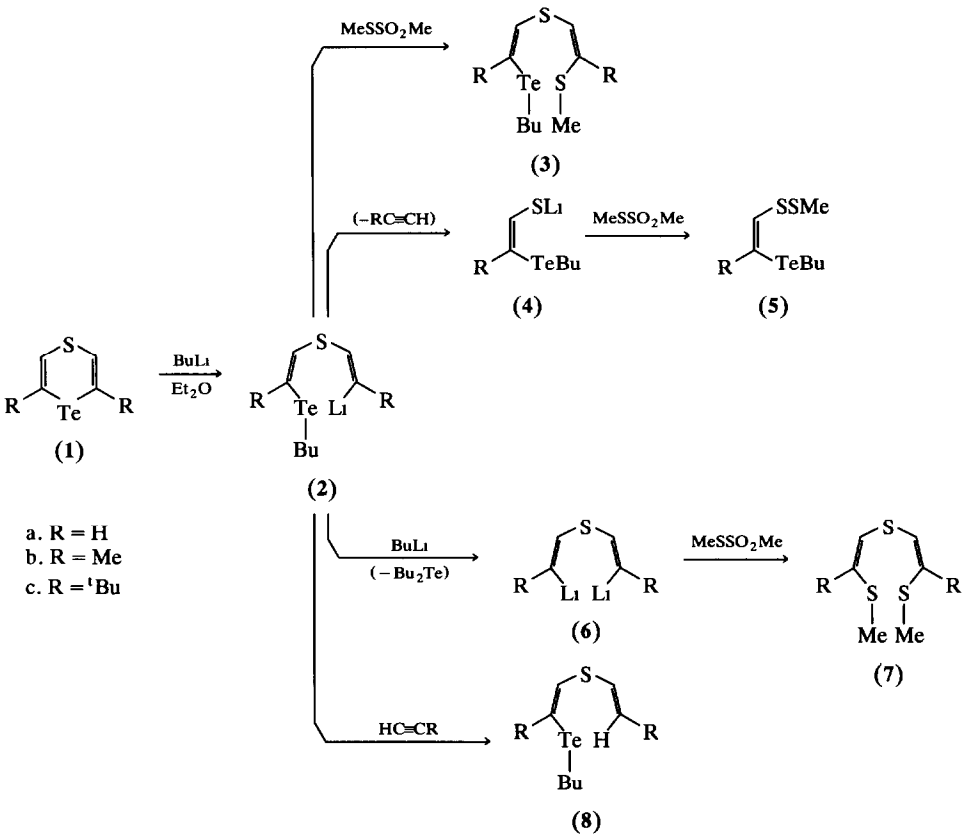
Reaction of 1,4-thiatellurin and some of its alkyl derivatives with *n*-butyllithium in tetrahydrofuran gives *Z,Z*-2,2′-dilithiodivinyl sulfide or alkyl derivatives and dibutyl telluride. With lithium diisopropylamide in tetrahydrofuran, in the case of 3,5′-dialkyl-1,4-thiatellurins, deprotonation with concomitant ring opening is the main reaction.

Introduction

Compared with their sulfur and selenium analogues, tellurium compounds show an increased sensitivity towards attack on the hetero atom in reactions with strongly basic reagents. This property has been exploited by Winter *et al.* [1] in the reaction of 2,5-diphenyltellurophene with *n*-butyllithium in diethyl ether in the presence of *N,N,N′,N′*-tetramethylethylenediamine. After hydrolysis of the product mixture and subsequent treatment with methyl iodide, *E,E*-1,4-diphenyl-1,3-butadiene and *E,E*-2,5-diphenyl-2,4-hexadiene were isolated. More recently, Hiro *et al.* [2] found that diorganyl tellurides TeR_2 can be cleaved by *n*-butyllithium in tetrahydrofuran to afford dibutyltelluride and a new organolithium compound RLi [2]. This cleavage is particularly useful for the generation of some aryl- and allyl-lithium derivatives and dilithium derivatives [3].

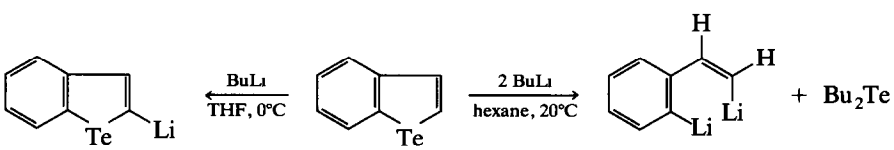
We recently [3] showed that the C–Te bonds in benzo[*b*]tellurophene are cleaved by n-butyllithium (BuLi) in hexane to give an elusive dilithium compound.

Correspondence to: Professor L. Brandsma.



Scheme 1.

In tetrahydrofuran (THF), α-lithiation is the only reaction.

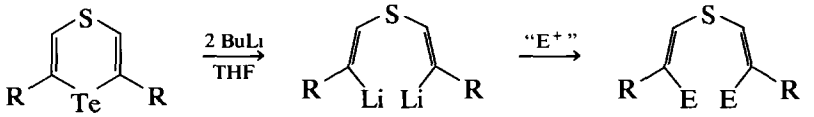


In the present paper we report similar selective transformations with 1,4-thiatellurins, compounds which were made several years ago [4].

Results and discussion

(a) 1,4-Thiatellurins + BuLi in diethyl ether and THF-Attack on Te (Schemes 1 and 2)

Addition of **1**, R = H (Scheme 1) to a solution of 2 equiv. of BuLi in ether followed by addition of methyl methanethiosulfonate afforded mixtures of dibutyl telluride, starting material, and compounds **3**, **5**, **7** and **8**. The ratio of the various compounds depended strongly on the temperature and the reaction time. At approx. −100°C, the conversion was fairly slow, and much of **1** was recovered; at



(1) (6) (7)

a. R = H
b. R = Me
c. R = ^{t}Bu

"E^+" = H_2O, MeI, $MeSSO_2Me$, Me_3SiCl, CO_2
E = H, Me, MeS, Me_3SiCl, COOH

Scheme 2.

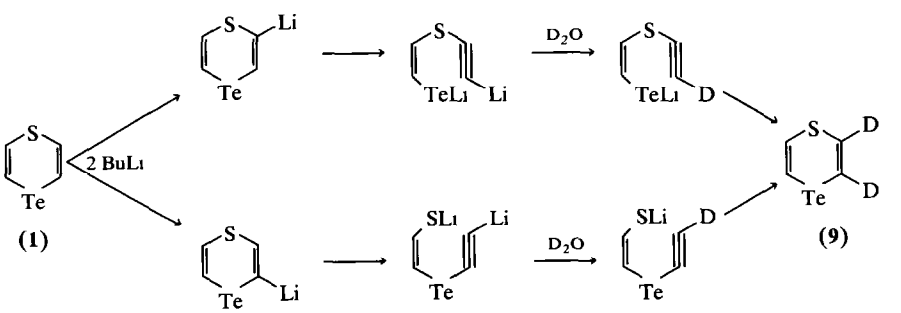
temperatures above 0°C, product **5** and butyl telluride predominated. The various reactions are depicted in Scheme 1.

The successive intermediates **2** and **6** resulting from attack of BuLi on tellurium apparently have a very low thermal stability, and so are not detected (as methylthio derivatives) when the reaction with BuLi is carried out at 0°C or higher temperatures. At very low temperatures, relatively more of **3** and **8** are formed, through methylthiolation and protonation (presumably by the acetylene eliminated from **2**) of **2**, the initial intermediate.

Similar experiments with **1**, R = Me and ^{t}Bu also gave mixtures of products, including butyl telluride and compounds formed by elimination of RC≡CH from **2** and **6** and subsequent methylthiolation.

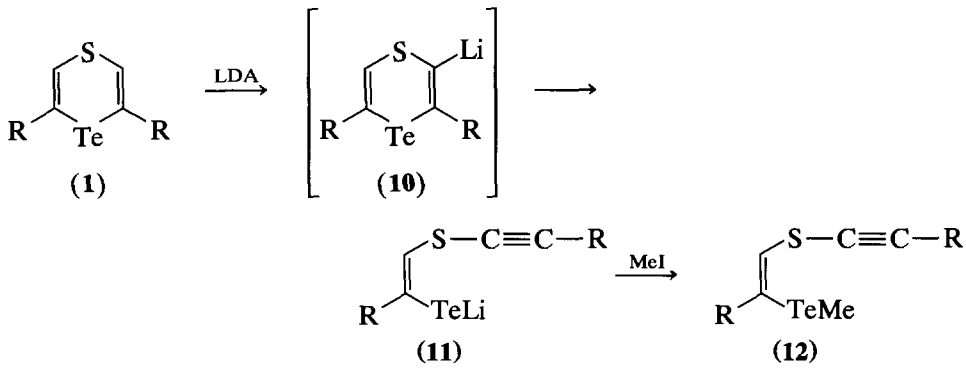
In the more polar solvent THF, the attack of BuLi on Te was much faster. At −105°C with 2 equiv. of the base, the formation of **6** (R = H, Me or ^{t}Bu) was complete after 5 (R = H) and 15 min (R = Me, ^{t}Bu), respectively. At this low temperature, **6** is sufficiently stable to allow successful derivatization with a variety of electrophiles (Scheme 2).

All products were formed in good yields. As expected, the products with R = H were pure *Z,Z*-divinyl sulfides. For R = Me and ^{t}Bu, the stereochemistry of the intermediates **6** was proven by hydrolysis, which gave pure *E,E*-divinyl sulfides.



R = H

Scheme 3.



Scheme 4.

(b) Reaction of 1,4-thiatellurin with BuLi and TMEDA in THF: deprotonation (+ring opening) and attack on tellurium (Schemes 3 and 1)

When the parent compound **1** was treated at −105°C with 2 equiv. of BuLi in THF in the presence of tetramethylethylenediamine (TMEDA) and deuterium oxide was added after 10 min, a mixture of 2,3-deuterated **1**, dibutyl telluride, *Z,Z*-dideuterodivinyl sulfide and divinyl sulfide was obtained. The ratio of 2,3-dideutero-1,4-thiatellurin **9** to dibutyl telluride was *ca.* 1:2.

The formation of the dideutero-compound **9** is presumably the result of ring metallation followed by a very fast eliminative ring opening and subsequent ring closure upon addition of D_2O. The initial ring deprotonation can, in principle, take place adjacent to sulfur or tellurium (*cf.* [5]). Dibutyl telluride, *Z,Z*-dideuterodivinyl sulfide and divinyl sulfide arise from attack on tellurium, the latter compound presumably by protonation of **6** (Scheme 1) by the eliminated acetylene.

(c) 1,4-Thiatellurins and lithium diisopropylamide in THF: deprotonation and ring opening (Scheme 4)

Since lithium diisopropylamide (LDA) was not expected to attack at tellurium we hoped to achieve deprotonation of **1** selectively by using a solution of this reagent in THF. However, interaction between 2 equiv. of LDA and **1**, R = H at 0°C gave, after methylation, only a small amount of tarry material. Under similar conditions **1**, R = Me and ^{t}Bu afforded the unsaturated tellurides **12** in good yields and high purity.

Under the conditions used the intermediates **10** are apparently unstable, and so an immediate ring opening occurs to give **11**, which is isolated as the methylation product **12**. At lower temperatures the conversion of **1** was incomplete, but subsequent reaction with methyl iodide did not give any methylation products of **10**.

Conclusion

Stereochemically pure 2,2′-disubstituted divinyl sulfides can be obtained in good yields by treatment of 1,4-thiatellurins with 2 equiv. of BuLi in THF at low temperatures, followed by addition of electrophiles. Under more polar conditions,

i.e. in the presence of TMEDA, ring-metallation by BuLi and concomitant ring opening competes with attack of BuLi on tellurium. When treated with LDA/THF, 3,5″-dialkyl-1,4-thiatellurins undergo ring lithiation with concomitant ring opening.

Experimental details

Analysis and characterization of the products were carried out by GLC, GC-MS and NMR spectroscopy (Varian EM-390 spectrometer). The Te-containing products were easy to recognize in the mass spectrum because of the characteristic isotope pattern.

Reaction of 1,4-thiatellurins **1** *(R = H, Me, ^{t}Bu) with ^{n}BuLi in THF and subsequent derivatization (yields of the products generally > 60%)*

A solution of 21 mmol of ^{n}BuLi in 13 ml of hexane was added dropwise at −105°C during 15 min to a well-stirred solution of **1** (10 mmol) in 100 ml of THF. After 10 (R = H) or 15 min (R = Me or ^{t}Bu), the resulting solution of **6** (Scheme 2) was treated with the relevant electrophile.

(1) Hydrolysis of **6**, *R = Me and ^{t}Bu.* A mixture of 2 g of water and 20 ml of THF was added with vigorous stirring, the temperature being kept below −100°C. The ratio of *E,E*-$(RCH{=}CH)_2S$ and Bu_2Te was *ca.* 1:1. To remove Bu_2Te the solution was stirred for 1 h at 20°C with 100 mmol of MeI. After washing of the solution with water and drying of the organic phase over $MgSO_4$, most of the THF was distilled off at atmospheric pressure.

NMR spectrum of *E,E*-$(MeCH{=}CH)_2S$ (undistilled): δ 5.90 (dq, H, SCH=C); δ 5.66 (dq, 1 H, S–C=CH); ^3J(H–C=CH) = 15.0 Hz; ^3J(HC–CH) = 6.2 Hz; ^4J(H–C–C=CH) = 0.9 Hz. NMR spectrum of *E,E*-$(^t BuCH{=}CH)_2S$ (b.p. 100°C/12 mmHg, n_D^{20} 1.4889, purity 99% by GLC): δ 5.83 (d, 1 H, SCH=C); 5.70 (d, 1 H); ^3J(HC=CH) = 15.5 Hz; 1.06 (s, 9 H, ^{t}Bu).

(2) Methylation. After addition of 100 mmol (large excess) of MeI at −105°C, the temperature was allowed to rise and the mixture stirred for 1 h at 20°C and then hydrolyzed. After work-up as described above the following products were obtained.

Z,Z-$(MeCH{=}CH)_2S$ (not purified by distillation). NMR spectrum: δ 5.98 (dq, 1 H, S–CH=C); 5.61 (dq, 1 H, S–C=CH); ^3J(H–C=CH) = 9.4 Hz; ^3J(H–C–C–H) = 6.6 Hz; ^4J(H–C–C=CH) = 1.3 Hz. $((Me)_2C{=}CH)_2S$ (b.p. 70°C/ 12 mmHg, n_D^{20} 1.5129, purity by GLC 95%): NMR spectrum: δ 5.63 (qq, 1 H); ^4J(HC–C=CH) = 1.3 Hz; 1.76 (3 H, CH_3); 1.70 (3 H, CH_3), second order pattern. $((Me)(^t Bu)C{=}CH)_2S$ (b.p. 131°C/12 mmHg, n_D^{20} 1.5081, purity 97% by GLC). NMR spectrum: δ 5.73 (q, 1 H); 1.69 (d, 3 H, CH_3); ^4J(H–C–C=C–H) = 0.9 Hz.

(3) Methylthiolation. A solution of methyl methanethiosulfonate (20 mmol) in 10 ml of THF was added during 1 min at −105 to −100°C. After 15 min, 100 mmol of MeI were added and the solution was stirred for 1 h at +20°C. After aqueous work-up, the following products were obtained.

Z,Z-$(MeSCH{=}CH)_2S$ (b.p. 60°C/0.25 mmHg, n_D^{20} 1.6420, purity 99% by GLC). NMR spectrum: δ 6.10 (S, 2 H, CH=CH); 2.32 (s, 3 H, SMe). $((Me)(MeS)C{=}CH)_2S$ (m.p. 41°C, after crystallization from cold pentane). NMR spectrum: δ 5.97 (q, 1 H); 2.25 (s, 3 H, SMe); 2.03 (d, 3 H, Me); ^4J(H–C–C=C–H) = 1.3 Hz.

((^{t}Bu)(MeS)C=CH)$_2$S (m.p. 77°C, after crystallization from cold pentane). NMR spectrum: δ 6.54 (s, 1 H); 2.25 (s, 3 H, SMe); 1.18 (s, 9 H, ^{t}Bu).

(4) Trimethylsilylation. Redistilled trimethylchlorosilane (30 mmol) was added during 1 min at −105°C. After 45 min stirring at −105°C, 100 mmol of MeI was added and the mixture was stirred for 1 h at 20°C. The usual work-up gave the following products. .

Z,Z-(Me$_3$SiCH=CH)$_2$S (b.p. 50°C/0.25 mmHg, n_D^{20} 1.4950, purity 95% by GLC). NMR spectrum: δ 7.09 (d, 1 H); 5.80 (d, 1 H); ^3J(H–C=CH) = 13.3 Hz; 0.18 (s, 9 H, Me$_3$Si). ((Me)(Me$_3$Si)C=CH)$_2$S (b.p. 67°C/0.3 mmHg, n_D^{20} 1.5050, purity 98% by GLC). NMR spectrum: δ 6.53 (q, 1 H); 1.83 (d, 3 H, Me); ^4J(H–C–C=C–H) = 1.6 Hz. ((^{t}Bu)(Me$_3$Si)C=CH)$_2$S was not formed, presumably due to steric hindrance.

(5) Carboxylation. A slow stream of carbon dioxide (*ca.* 300 ml/min) was passed at −105°C for 10 min into the solution of **6**. Water was then added with vigorous stirring. The aqueous phase was extracted three times with diethyl ether and subsequently acidified (2 *M* HCl) to pH 1. The acid was isolated by extraction with diethyl ether (8 times), drying of the extracts over MgSO$_4$, and concentration *in vacuo*. The following acids were obtained.

Z,Z-(HOOC–CH=CH)$_2$S (white solid, decomposition upon heating, purity ~ 95% by NMR). NMR spectrum (acetone-d_6 as solvent): δ 7.60 (d, 1 H); 6.01 (d, 1 H); ^3J(H–C=C–H) = 10.3 Hz. ((Me)(COOH)C=CH)$_2$S (white solid, m.p. not determinable). NMR-spectrum (acetone-d_6 as solvent): δ 7.26 (q, 1 H); 1.97 (d, 3 H, Me); ^4J(H–C–C=C–H) = 1.3 Hz. ((^{t}Bu)(COOH)C=CH)$_2$S (white solid, m.p. not determinable). NMR spectrum (acetone-d_6 as solvent): δ 7.02 (s, 1 H); 1.23 (s, 9 H, ^{t}Bu).

Reaction of 1,4-thiatellurines 1 (R = Me, ^{t}Bu) with LDA in THF

To a solution of 12 mmol of LDA in 75 ml of THF at −60°C was added a solution of 10 mmol of the thiatellurin in 5 ml of THF. The temperature of the mixture was allowed to rise to 10–20°C and after a further 15 min, 20 mmol of MeI was added at −60°C and the temperature was allowed to rise to 10–20°C. After a further 30 min, water was added and the products isolated in the usual way. The following compounds (purity by NMR ≥ 97%) were isolated.

MeC≡C–CH=C(Me)TeMe (b.p. 95°C/0.25 mmHg, n_D^{20} 1.6540), yield ~ 75%. NMR spectrum: δ 6.38 (qq, 1 H); ^3J(^{125}Te–C=C–H) = 16.2 Hz; 2.22 (d, 3 H, C=C–CH$_3$); ^4J(H–C–C=C–H) = 1.5 Hz; 1.98 (d, 3 H, TeCH$_3$); ^2J(^{125}Te–C–H) = 24.8 Hz; ^5J(H–C–Te–C=C–H) = 0.4 Hz; 1.94 (s, 3 H, C≡C–CH$_3$). ^{t}BuC≡C–CH=C(^{t}Bu)–TeMe (m.p. 50–51°C after crystallization from cold pentane), yield ~ 80%. NMR spectrum: δ 6.53 (s, 1 H); ^3J(^{125}Te–C=C–H) = 6.0 Hz; 1.95 9s, 3 H, TeCH$_3$); ^2J(^{125}Te–C–H) = 24.0 Hz; 1.25 (s, 9 H, C≡C–^{t}Bu); 1.17 (s, 9 H, C=C–^{t}Bu).

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