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Tetrahedron Letters 45 (2004) 2981–2984

Tetrahedron Letters

Hydrotelluration and carbotelluration of acetylenic sulfoxides: regio- and stereoselective preparation of α- and β-organotellurovinyl sulfoxides

Qing Xu,[a] Xian Huang[a,b,*] and Jun Ni[a]

[a]*Department of Chemistry, Zhejiang University (Xixi Campus), Hangzhou 310028, PR China*
[b]*State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 354 Fenglin Lu, Shanghai 200032, PR China*

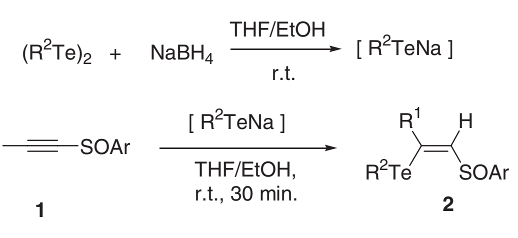
Received 23 October 2003; revised 28 January 2004; accepted 4 February 2004

Abstract—(*Z*)-β-Organotellurovinyl sulfoxides were synthesized via a highly regio- and stereoselective *anti*-hydrotelluration of acetylenic sulfoxides. α-Organotellurovinyl sulfoxides were obtained from a three component *syn*-carbotelluration reaction of acetylenic sulfoxides, that is, *syn*-addition of monoorganocopper reagents to acetylenic sulfoxides followed by the electrophilic reaction of the vinyl copper intermediates with benzenetellurenyl iodide at low temperature. Synthetic applications of the organotellurovinyl sulfoxides have been investigated.

Stereoselective synthesis of substituted alkenes has drawn a lot of attention in organic synthesis, in which the transformations of vinylic and acetylenic chalcogen compounds are one of the most efficient routes to stereodefined alkenes.[1] Vinyltellurides are especially important synthetic intermediates because of their ready conversion to other intermediates or compounds with excellent retention of the configuration.[1,2] Regio- and stereoselective preparation of α- and β-functionalized vinyl tellurides[3,4] are still hot topics of research because of their potential applications in organic synthesis.[1,5]

We are also interested in the synthesis and applications of stereo-defined functionalized vinyl chalcogenides.[6] Recently, our group has reported the *anti*-hydrotelluration of acetylenic sulfones and acetylenic phosphonates,[6i] free radical tellurosulfonation of acetylenes,[6i] selenomagenization of acetylenic sulfones,[6c,d] and selenolithiation of acetylenic phosphine oxides[6f] to prepare functionalized vinyl chalcogenides. On the other hand, substituted vinyl sulfoxides, especially the optically pure ones, are very important synthetic intermediates in organic synthesis[7] and we have studied the regio- and stereoselective hydrozirconation of acetylenic sulfoxides[8] to prepare substituted vinyl sulfoxides.[6b] As a part of our ongoing studies we wish to report the *anti*-hydrotelluration and three component *syn*-carbotelluration of acetylenic sulfoxides to prepare β- and α-organotellurovinyl sulfoxides, respectively.

Acetylenic sulfoxides were added to a EtOH/THF solution of sodium phenyltellurolate, prepared in situ from diorganoditelluride and sodium boronhydride, at room temperature to afford high yields of β-organotellurovinyl sulfoxides (Scheme 1).[9] The J value of the two vinyl protons in compound **2a** ($J = 9.20$ Hz) shows they are in a *syn*-relationship, which indicates the hydrotelluration of acetylenic sulfoxides is an *anti*-addition reaction.[10] Results of these reactions are summarized in Table 1.



Scheme 1.

Keywords: Organotellurovinyl sulfoxides; Hydrotelluration; Carbotelluration.

* Corresponding author. Fax: +86-571-88807077; e-mail: huangx@mail.hz.zj.cn

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doi:10.1016/j.tetlet.2004.02.064

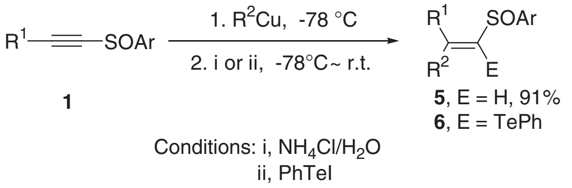
Table 1. Synthesis of (*Z*)-β-organotellurovinyl sulfoxides

Product	R^1	Ar	R^2	Yield (%)[a]
2a	H	*p*-Tol	Ph	85
2b	n-C_4H_9	*p*-Tol	Ph	93
2c	n-C_4H_9	Ph	Ph	89
2d	n-C_4H_9	Ph	n-C_4H_9	84
2e	n-C_5H_{11}	*p*-Tol	Ph	92
2f	n-C_5H_{11}	Ph	Ph	81
2g	n-C_6H_{13}	*p*-Tol	Ph	96
2h	n-C_6H_{13}	Ph	Ph	90

[a] Isolated yield based on acetylenic sulfoxide.

Notably, in the case of phenylacetylenyl aryl sulfoxides small amounts of the detellurolated side products (*E*)-phenylvinyl aryl sulfoxides **3a** and **3b** were obtained in addition to the main products **2i** and **2j** (Scheme 2). Compound **2i** and **2j** were found to be unstable and thus were quickly converted to dibromides **4** by the addition of 1.0 equiv of bromine in methanol at 0 °C.

α-Functionalized vinyl tellurides are another class of compounds that have received great recognition.[1,3] Therefore we also prepared α-organotellurovinyl sulfoxides. We found that use of an organocopper reagent[11] was a direct and efficient protocol to obtain such α-organotellurovinyl sulfoxides with predicted configuration. Literature reports[12] show that monoorganocopper reagents are not only more suitable Michael addition reagents to acetylenic sulfoxides than are diorganocopper reagent, but they also exhibit excellent regio- and stereochemistry. Therefore, we investigated the two component reaction of monoorganocopper reagents with acetylenic sulfoxides to examine the regio- and stereochemistry of these addition reactions (Scheme 3). When the addition reaction of the phenylcopper reagent prepared in situ from CuI and 1.0 equiv of phenylmagnesium bromide with butynyl *p*-tolyl sulfoxide at −78 °C was completed as monitored by TLC, the reaction mixture was quenched with saturated aqueous ammonium chloride at this temperature. High yield of the product **5** ($R^1 = n$-Bu, $R^2 = Ph$, $E = H$) was obtained after workup and purification. Spectroscopic data of **5** was found to be identical to the previous report,[7a] which indicates that the conjugate addition of monoorganocopper reagents to acetylenic sulfoxides is *cis*-specific, as reported.[12] The above *syn*-conjugate addition reaction was then applied to the synthesis of α-organotellurovinyl sulfoxides (Scheme 3).[13] After the *syn*-addition reaction of the monoorganocopper reagent to the acetylenic sulfoxides was completed, benzenetellurenyl iodide, prepared in situ from diphenyl ditelluride and iodine at 0 °C, was added dropwise at −78 °C. The α-organotellurovinyl sulfoxides were afforded in moderate to good yields as the sole product. The reaction of allyl copper reagents can also afford the expected products but with slightly lower yield (Product 6c). This might result from the different reactivity of allyl copper reagents compared to normal copper reagents since other undetermined products were also found. The results of these reactions are summarized in Table 2.



Scheme 3.

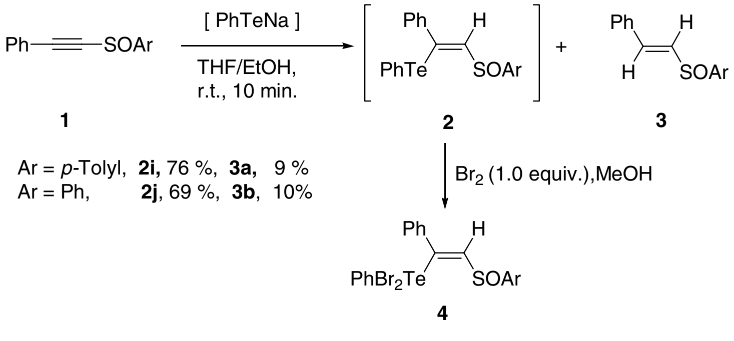
We postulated that the presence of the sulfinyl group in the acetylenic sulfoxides is the key factor for controlling the observed excellent regio- and stereoselectivity in the above *anti*-hydrotelluration and *syn*-carbotelluration reactions, since the electron withdrawing sulfinyl group is a relatively strong inductive group, just as sulfone and phosphonate groups are, and therefore they afford the products with controlled regio- and stereoselectivity.

With the organotellurovinyl sulfoxides in hand, we set out to study their applications in the preparation of poly-substituted vinyl sulfoxides, since the reactive tellurium group is a good precursor in many transforma-

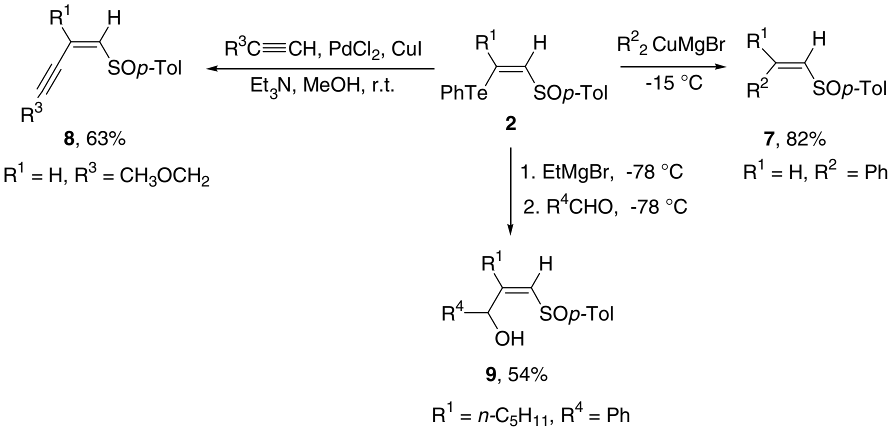
Table 2. Synthesis of α-organotellurovinyl sulfoxides

Product	R^1	R^2	Ar	Yield (%)[a]
6a	n-C_4H_9	Et	*p*-Tol	79
6b	n-C_4H_9	Ph	*p*-Tol	85
6c	n-C_4H_9	Allyl	*p*-Tol	34
6d	n-C_5H_{11}	Et	*p*-Tol	76

[a] Isolated yield based on acetylenic sulfoxide.



Scheme 2.



Scheme 4.

tions.[1,2,5] As shown in Scheme 4, the substitution reactions of (*Z*)-β-organotellurovinyl sulfoxides **2a** with diorganocopper reagents at −15 °C afforded good yields of vinyl sulfoxides **7** with the total retention of configuration. The *J* value of the two vinyl protons, $J = 10.40$ Hz, shows they are in a *syn*-relationship. Compound **2a** can also couple with terminal acetylenes in the presence of a catalytic amount of $PdCl_2$ and CuI in methanol to afford conjugate sulfinyl enyne **8** that also exhibit retention of configuration ($J = 10.0$ Hz). The Te/Mg exchange reaction of **2e** with ethyl magnesium bromide followed by the electrophilic reaction with benzaldehyde afforded sulfinyl group substituted allyl alcohol **9**. On the other hand, the sulfinyl group itself is a potential reaction center. It is not only a very good leaving group both in ionic[14] and free radical reactions,[15] but it can also undergo substitution reactions with several organometallic reagents.[16] Therefore, the above obtained vinyl sulfoxides are versatile intermediates with many potential synthetic uses.

In summary, we have developed efficient methods for the regio- and stereoselective preparation of α- and β-organotellurovinyl sulfoxides from the readily available acetylenic sulfoxides. Preliminary application studies have demonstrated the utility of organotellurovinyl sulfoxides as precursors for certain potentially useful compounds in organic synthesis.

Acknowledgements

We are grateful to the National Natural Science Foundation of China (Project Nos. 20272050, 20332060) for financial support.

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9. Typical procedure for the preparation of (*Z*)-β-organotellurovinyl sulfoxides **2**: Sodium boronhydride in EtOH was added dropwise to the solution of diorganoditelluride

(0.5 mmol) in THF (3 mL) under N_2. The characteristic dark-red color of the ditelluride gradually faded and turned to colorless, and then acetylenic sulfoxide in THF was added and the mixture was stirred at room temperature for 30 min, quenched with saturated aqueous NH_4Cl, and extracted with EtOAc. The organic phase was dried over sodium sulfate and concentrated under vacuum. The residue was purified by preparative TLC on silica gel (eluent: AcOEt:*n*-hexane = 1:5) to give compounds **2** in high yields.

10. Selected data of compound **2a**: Pale yellow solid, mp 73–75 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 7.88–7.86 (d, $J = 9.20$ Hz, 1H), 7.83–7.81 (dd, $J = 0.80$ Hz, $J = 8.0$ Hz, 2H), 7.66–7.64 (d, $J = 8.0$ Hz, 2H), 7.36–7.28 (m, 5H), 7.02–7.00 (d, $J = 9.20$ Hz, 1H), 2.43 (s, 3H). ^{13}C NMR (400 MHz, $CDCl_3$): δ 142.8, 140.2, 138.4, 132.8, 13.06, 129.8, 128.5, 125.6, 120.7, 119.8, 22.0. MS (EI) *m*/*z* (%) 372 (18, M^+), 356 (2), 265 (17), 207 (10), 165 (10), 139 (43), 123 (6), 91 (32), 77 (100). IR (KBr) cm^{-1} 3052, 2922, 1594, 1574, 1545, 1492, 1475, 1435, 1399, 1327, 1180, 1143, 1120, 1080, 1032, 1014, 910. Anal. Calcd for $C_{15}H_{14}OSTe$: C, 48.70; H, 3.814. Found: C, 48.45; H, 3.853.
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13. Typical procedure for the preparation of α-organotellurovinyl sulfoxides **6**: Alkyl or aryl magnesium bromide (0.75 mmol) in dry THF or ether was added at 0 °C to the THF suspension of CuI (0.75 mmol) in a tube reactor under nitrogen to form the monoorganocopper reagents. The mixture was then cooled to −78 °C and the acetylenic sulfoxide (0.5 mmol) in dry THF was injected with a syringe. The reaction mixture was stirred at a temperature not higher than −50 °C for 1 h and then was cooled to −78 °C again. Bezenetellurenyl iodide (0.75 mmol), prepared in situ from diphenyl ditelluride and iodine in THF at 0 °C, was then added dropwise. After the temperature was gradually returned to room temperature, the mixture was washed with saturated aqueous NH_4Cl and NaCl, abstracted with EtOAc, dried over $MgSO_4$. The solvent was evaporated and the residue purified by TLC to afford the product **6**. Selected data of compound **6b**: Pale yellow solid, mp 104–106 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 7.61–7.59 (d, $J = 8.40$ Hz, 2H), 7.32–7.30 (d, $J = 8.00$ Hz, 2H), 7.22–7.12 (m, 3H), 7.08–7.04 (m, 1H), 6.92–6.89 (m, 2H), 6.86–6.80 (m, 4H), 3.35–3.28 (m, 1H), 2.97–2.90 (m, 1H), 2.43 (s, 3H), 1.46–1.33 (m, 4H), 0.91–0.87 (t, $J = 7.20$ Hz, 3H). ^{13}C NMR (400 MHz, $CDCl_3$): δ 163.31, 143.03, 141.38, 138.96, 135.99, 129.96, 128.73, 128.14, 128.03, 127.90, 127.57, 125.41, 114.85, 38.10, 30.97, 22.81, 21.85, 14.22. MS (EI) *m*/*z* (%) 505 (M^++1, 6), 504 (M^+, 2), 427 (2), 397 (2), 314 (7), 207 (9), 157 (100), 139 (15), 129 (16), 115 (21), 103 (7), 91 (29), 77 (39). IR (KBr) cm^{-1} 3053, 2956, 2926, 2860, 1573, 1490, 1473, 1434, 1379, 1301, 1082, 1048, 1017, 998, 912. Anal. Calcd for $C_{25}H_{26}OSTe$: C, 59.80; H, 5.219. Found: C, 59.43; H, 5.261.
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