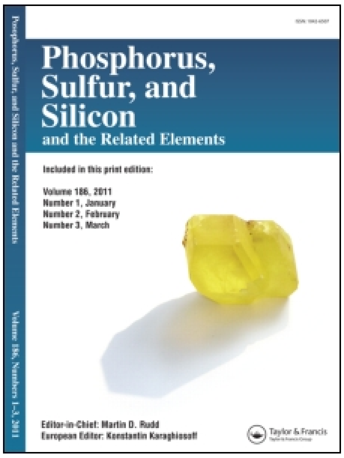


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Synthesis and Reaction of Vinylic Tellurides

Jun Terao; Nobuaki Kambe; Noboru Sonoda

To cite this Article Terao, Jun , Kambe, Nobuaki and Sonoda, Noboru(1998) 'Synthesis and Reaction of Vinylic Tellurides', Phosphorus, Sulfur, and Silicon and the Related Elements, 136: 1, 637 — 640

To link to this Article: DOI: 10.1080/10426509808546014

URL: http://dx.doi.org/10.1080/10426509808546014

Phosphorus Sulphur and Silicon
Vols. 136, 137 & 138 pp. 637-640
Reprints available directly from the publisher
Photocopying permitted by license only

Published by license under the
Gordon and Breach Science Publishers imprint
Printed in Malaysia

SYNTHESIS AND REACTION OF VINYLIC TELLURIDES

JUN TERAO[a], NOBUAKI KAMBE[a], and NOBORU SONODA[b]
[a]Department of Applied Chemistry, Faculty of Engineering, Osaka University, Suita, Osaka 565 Japan; [b]Department of Applied Chemistry, Faculty of Engineering, 3-3-35 Yamatecho, Kansai University, Suita, Osaka 564 Japan

Vinylic tellurides were synthesized by the addition of diorganyl tellurides to acetylenes in the presence of a radical initiator or by visible light irradiation. Vinylic tellurides underwent transmetalation by the reaction with triethylaluminium or diethylzinc to form the corresponding vinylmetal reagents with retention of the double bond configuration. Oxidation of vinylic tellurides formed by carbotelluration reactions followed by pyrolysis gave internal acetylenes in good yields.

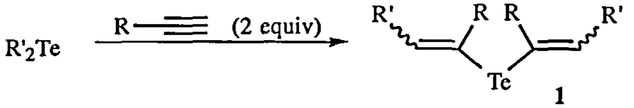
Keywords: vinylic tellurides; divinyl tellurides; Te-Zn exchange reaction; Te-Al exchange reaction; oxidation of vinylic tellurides

INTRODUCTION

Vinylic tellurides are synthetically very useful compounds especially for introduction of vinyl moieties into organic molecules with carbon-carbon bond formation.[1] We have recently developed a carbotelluration reaction of acetylenes in the presence of a radical initiator to form vinylic tellurides via S_H2 reaction at the tellurium atom.[2] Herein, we present a new preparative method of divinyl tellurides by visible light irradiation and some synthetic application of vinylic tellurides formed by carbotelluration.

Synthesis of Divinyl Tellurides via Carbotelluration Reaction

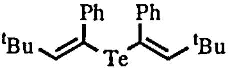
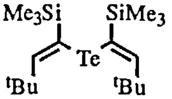
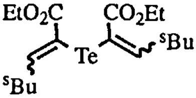
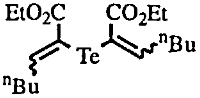
Since alkyl substituted tellurides show absorption in the range of $\lambda > 300$ nm assignable to n-σ^* transition[3] which can lead to cleavage of Te-C bonds,[3a] we used a tungsten lump as the light source. Under the irradiation with a tungsten lump at 50 ℃, symmetrical tellurides reacted with 2 equiv of acetylenes to form divinyl tellurides **1** (eq. 1).



1 (1)

Tellurides having secondary and tertiary alkyl substituents afforded divinyl tellurides in moderate to good yields, whereas $^{n}\mathrm{Bu_2Te}$ gave only a poor yield of the product (Table 1). This is in good agreement with the order of stabilities of radicals formed by photolysis and/or that of facilities of the S_H2 reaction on tellurium. Reactions of $^{t}\mathrm{Bu_2Te}$ with phenyl- and trimethylsilyl acetylenes proceeded stereoselectively giving rise to only *EE* and *ZZ* products, respectively (runs 1 and 2).

TABLE I Synthesis of divinyl telluride.

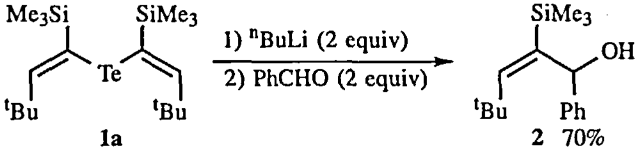
Entry	Telluride	Acetylene	Divinyl telluride	Yield[a] (%)	*EE/EZ/ZZ*[b]
1	$^{t}\mathrm{Bu_2Te}$	Ph—≡		86	*EE* only
2	$^{t}\mathrm{Bu_2Te}$	$\mathrm{Me_3Si}$—≡		76	*ZZ* only
3	$^{s}\mathrm{Bu_2Te}$	$\mathrm{EtO_2C}$—≡		43	20/52/28
4	$^{n}\mathrm{Bu_2Te}$	$\mathrm{EtO_2C}$—≡		8	29/50/21

---

[a] Isolated yield based on tellurides used. [b] Determined by ^{1}H NMR and/or GC.

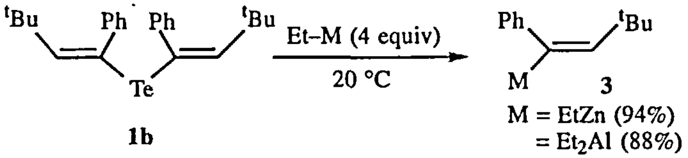
Tellurium-Metal Exchange Reactions

Diorganyl tellurides undergo tellurium-metal exchange reaction by the treatment with various organometallic reagents (metal = Li[4a], Na[4b], K[4b], Mg[4b], Ca[4b], Cu[4c], Zn[4d], Al[4e]). For example, **1a** reacts with 2 equiv of butyllithium to give the corresponding vinyllithium, which can be trapped with benzaldehyde leading to allylic alcohol **2** with complete retention of the stereochemistry in 70% yield based on the vinyl groups of **1a** (eq. 2).



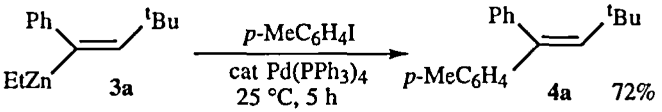
(2)

Divinyl telluride **1b** also reacts with diethylzinc or triethylaluminum at room temperature to give corresponding vinylmetal compounds **3** in high yields (eq. 3).

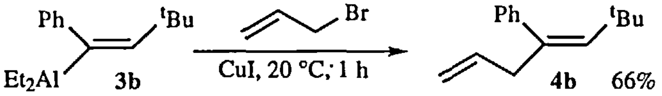


(3)

These vinylzinc and vinylaluminum compounds were subjected to the cross-coupling reaction with various halides to give corresponding products **4a,b** as a single stereoisomer (eqs. 4, 5).[4d,4e,5]



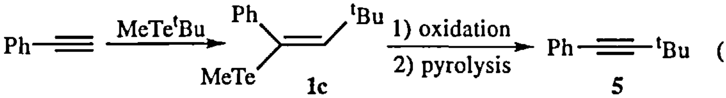
(4)



(5)

Synthesis of Internal Acetylenes by Vinylic Tellurides

It is known that telluroxides and tellurones undergo elimination reaction to give olefins[6] as in the cases of selenoxides. Here we disclose that internal acetylenes are formed in good yields by pyrolysis of vinylic telluroxide or tellurones. Oxidation of vinylic telluride **1c** with an aqueous sodium hypochlorite followed by heating at 250 ℃ in vacuo gave the corresponding internal acetylene **5** in 88% yield. Combination of this reaction with carbotelluration provides a useful method for introduction of tert-alkyl groups to terminal acetylenes.



(6)

References

[1.] For recent reviews, see: J. V. Comasseto, L. W. Ling, N. Petragnani, H. A. Stefani, *Synthesis* 373 (1997). J. V. Comasseto, *Rev. Heteroatom Chem.* **9**, 61 (1993).

[2.] L.-B. Han, K. I. Ishihara, N. Kambe, A. Ogawa, I. Ryu, N. Sonoda, *J. Am. Chem. Soc.* **114**, 7591 (1992).. L.-B. Han, K. I. Ishihara, N. Kambe, A. Ogawa, N. Sonoda, *Phosphorous, Sulfur, and Silicon* **67**, 243 (1992).

[3.] a) K. T. Higa, D. C. Harris, *Organometallics* **8**, 1674 (1989). b) R. W. Gedrige, K. T. Higa, D. C. Harris, R. A. Nissan, M. P. Nadler, *Organometallics* **8**, 2812 (1989).

[4.] a) T. Hiiro, N. Kambe, A. Ogawa, N. Miyoshi, S. Murai, N. Sonoda, *Angew. Chem.* **99**, 1221 (1987). b) T. Kanda, T. Sugino, N. Kambe, N. Sonoda, *Phosphorous, Sulfur, and Silicon* **67**, 103 (1992). c) F. C. Tucci, A. Chieffi, J. V. Comasseto, *Tetrahedron Lett.* **33**, 5721 (1992). d) J. Terao, N. Kambe, N. Sonoda, *Tetrahedron Lett.* **37**, 4741 (1996). T. Studemann, V. Gupta, L. Engman, P. Knochel, *Tetrahedron Lett.* **38**, 1005 (1997). e) J. Terao, N. Kambe, N. Sonoda, *Synlett* 779 (1996).

[5.] E. I. Negishi, F. T. Luo, *J. Org. Chem.* **48**, 1560 (1983). E. Erdik, *Tetrahedron* **48**, 9577 (1992). R. A. Lynd, G. Zweifel, *Synthesis* 658 (1974).

[6.] K. B. Sharpless, K. M. Gordon, R. F. Lauer, D. W. Patrick, S. P. Singer, M. W. Young, *Chem. Scr.* **8A**, 9 (1975). H. Lee, M. P. Cava, *J. Chem. Soc., Chem. Commun.* 277 (1981). .S. Uemura, S. I. Fukuzawa, *J. Am. Chem. Soc.* **105**, 2748 (1983).