Pergamon

Tetrahedron Letters 39 (1998) 5511–5512

TETRAHEDRON
LETTERS

# Synthesis of Internal Acetylenes from Vinylic Tellurides

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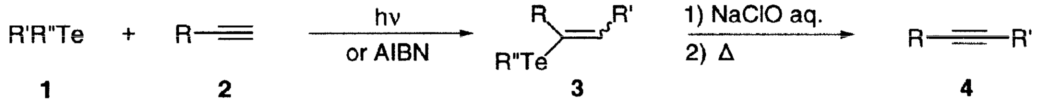
Received 21 April 1998; revised 19 May 1998; accepted 22 May 1998

## Abstract

Vinylic tellurides were prepared by carbotelluration of acetylenes under light. The subsequent oxidation with sodium hypochlorite followed by pyrolysis gave internal acetylenes in good yields. Combination of these reactions provides a useful method for introduction of alkyl groups to terminal acetylenes.

*Keywords*: Vinylic tellurides; Oxidation; Internal acetylenes; Carbotelluration

The *syn* elimination of selenoxides is an important reaction for construction of carbon-carbon double bond functionalities.[1] In contrast to this well-developed selenium chemistry, similar transformation of the tellurium analogue is much less explored. The telluroxide elimination reaction was first examined by Sharpless et al,[2] and the synthetic utility of this reaction for double bond formation has been demonstrated by Uemura et al.[3,4] We report here the first example of the formation of internal acetylenes from vinylic tellurides, which have been prepared by addition of tellurides to terminal acetylenes.



When mixtures of tellurides (**1**) having a *tert*-Bu group and terminal acetylenes (**2**, 1.2 equiv) were irradiated at 50 °C using a tungsten lamp, carbotelluration proceeded regio- and stereoselectively to give vinylic tellurides (**3a-d**) in good yields (Figure 1).[5] Telluride **3e** was prepared using AIBN as a radical initiator according to the literature.[6] Into a $CHCl_3$ solution (5 mL) of vinylic telluride **3** (2 mmol) was added an aqueous sodium hypochlorite solution (5-8 equiv) at 25 °C, and the mixture was stirred for 30 min. The products were extracted with $CHCl_3$, and the extract was dried over $MgSO_4$, concentrated, and heated gradually in a Kugelrohr distillation apparatus up to 250 °C *in vacuo*, giving rise to the corresponding internal acetylenes (**4**). The structures and yields of **4** together with the corresponding starting vinylic tellurides (**3**) are shown in Figure 1.

*PII:* S0040-4039(98)01085-5

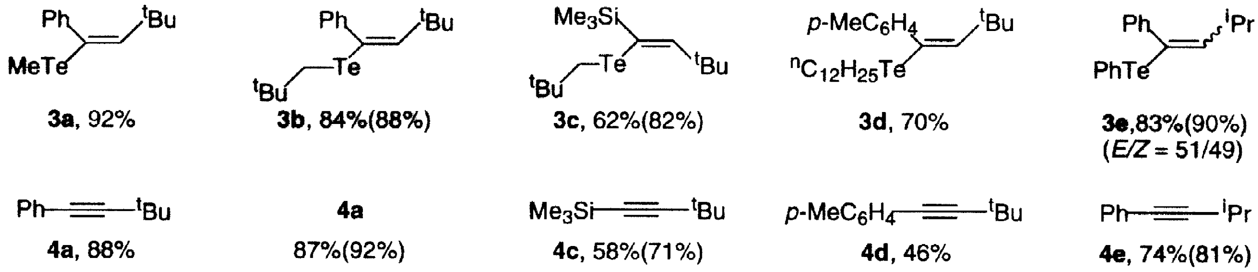
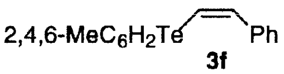
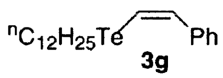


**Figure 1**. Structures and isolated yields (NMR yield) of products.

Acetylenes were formed in good yields from vinylic tellurides having no β-hydrogen on the $sp^3$-carbon (**3a-c,e**). Similar satisfactory results were obtained when $H_2O_2$ or $^tBuOOH$[2] was employed as the oxidizing reagent, whereas oxidation with $^tBuOCl/NaHCO_3$[7] and $Br_2/NaOH$[3] afforded only moderate to poor yields of acetylenes partly due to an undesirable reaction with the double bonds. It should be noted that the β-hydrogen located *trans* to the tellurium can be removed in this elimination as demonstrated by the reactions of **3c** and **3e** (ca. 1:1 mixture of stereoisomers), which gave **4c** in 58% and **4e** in 74% yields, respectively. The use of **3d** afforded 46% yield of **4d** along with 38% of 1-dodecene, indicating that the abstraction of the *syn* hydrogen on the $sp^2$ β-carbon leading to **4d** competes with that on the $sp^3$ β-carbon giving rise to the olefin. Similar reactions of **3f** and **3g**, prepared by a literature procedure,[8] gave phenylacetylene (75%) and 1-dodecene (62%) as the sole product, respectively. These results indicate that the vinylic hydrogen located *trans* to the tellurium is removed much more slowly than the double bond formation.



**3f**



**3g**

In conclusion, we have found that both *cis* and *trans* vinylic tellurides could be converted to internal acetylenes by an oxidation-pyrolysis sequence. Combined use of this elimination reaction with photo-promoted carbotelluration of terminal acetylenes provides a useful method for formation of internal acetylenes, since direct introduction of a *tert*-alkyl group on the terminal carbon of acetylenes can not easily be attained.[9]

## References and Notes

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