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Coupling of Z-vinylic tellurides with alkynes catalysed by $PdCl_2$/CuI: synthesis of Z-enynes and Z-enediynes

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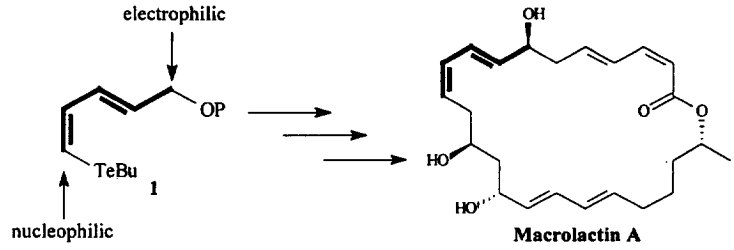
Abstract

Vinylic tellurides of the Z-configuration couple with alkynes under $PdCl_2$/CuI catalysis to give enynes and enediynes in good yields and with retention of the double bond configuration. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: vinylic tellurides; enynes; enediynes.

The easy access to vinylic tellurides of defined geometry and their transformation into highly reactive organometallics[1] with retention of the olefin geometry can transform this class of compounds into an advantageous alternative to the existing methods for preparing vinyllithiums,[2] vinylcuprates[3] and vinylzinc chlorides[4] through transmetallation reactions. The usefulness of these transformations was recently demonstrated when the bifunctional reagent **1** (Scheme 1) was succesfully employed in the first step of the enantioselective synthesis of macrolactins,[5] a class of antiviral macrolactones.[6]



Scheme 1.

Another application of the transmetallation reaction of vinylic tellurides is their transformation into mixed vinyl copper–zinc compounds followed by coupling with bromoalkynes, giving rise to Z-enynes and Z-enediynes,[7] present in several potent antitumor antibiotics. In view of the success of these transformations we decided to investigate catalytic methods of carbon–carbon bond formation

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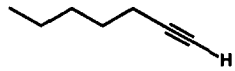
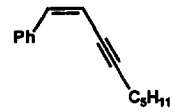
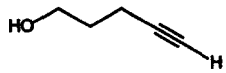
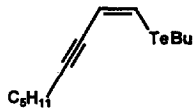
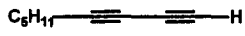
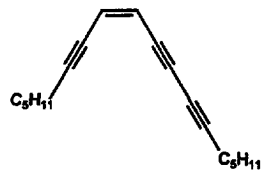
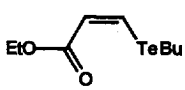
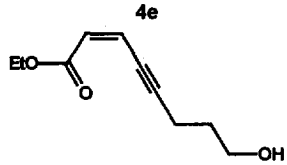
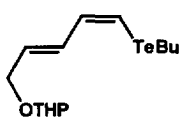
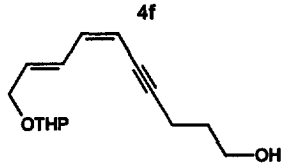
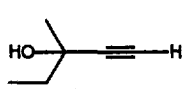
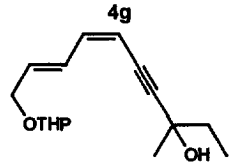
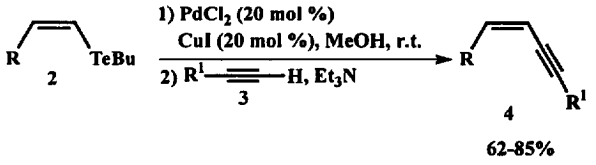
Table 1
Enynes and enediynes prepared

Vinylic Telluride[a]	Alkyne	Product[b]	Reaction Time (h)	Yield (%)[c]
 2a	 3a	 4a	4	85
2a	 3b	 4b	3	73
 2b	3b	 4c	4	75
2b	 3c	 4d	5	70
 2c	3b	 4e	3	83
 2d	3b	 4f	1	62
 2e	3b	 4g	3	78
2e	 3d	 4h	5	74

[a]Prepared by literature methods[11]; [b]The analytical data agree with the proposed structures; [c]Yield of the product purified by column chromatography.

involving vinylic tellurides. In this communication we report a stereospecific catalytic carbon–carbon bond formation involving vinylic tellurides.

Experimentally, the reaction was very easily performed by adding the vinylic telluride to a mixture of $PdCl_2$ and CuI in dry methanol. To this mixture were added an alkyne and triethylamine. The reaction was exothermic and the temperature was controlled by means of a water bath (Eq. 1).[8]



(1)

The reaction occurred with retention of the double bond geometry as demonstrated by the coupling constants of the vinylic protons (10.6–11.9 Hz) of the coupled products **4** (Table 1). It is worth noting the compatibility of the hydroxyl and ester groups to the reaction conditions employed. The present method constitutes an improvement of the previous one published by us, which employed mixed vinylzinc/copper species to perform the sp–sp_2 carbon–carbon bond formation.[7] In addition, an alkyne instead of a haloalkyne was used in the coupling step. Depending on the structure of the vinylic telluride used, enynes or enediynes were obtained. Keeping in mind the easy and highly regio- and stereoselective hydrotelluration of diynes, which occurs under mild conditions,[9] the sequence hydrotelluration/catalytic vinylic telluride coupling constitutes one of the most straightforward and versatile methods of assembling functionalized *Z*-enediynes moieties.[10]

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8. Typical procedure for the coupling reaction: to a two-necked 25 mL round-bottomed flask under N_2 atmosphere containing $PdCl_2$ (0.035 g, 20 mmol%), CuI (0.040 g, 20 mmol%) and dry methanol (5 mL) was added the vinylic telluride **2a** (0.143 g, 0.5 mmol). After stirring the mixture for 15 min at room temperature, were added 1-heptyne **3a** (0.096 g, 1 mmol) and Et_3N (0.3 mL). The reaction was exothermic and the temperature was maintained between 15–20°C by using a water bath. The stirred reaction was kept at room temperature for the times indicated in Table 1. Then the solid part was filtered and

the filtrate was treated with saturated solution of NaCl (30 mL). The aqueous layer was extracted with ethyl acetate (3×20 mL), the combined organic layers were dried over $MgSO_4$ and concentrated under vacuum. The residue was purified by silica gel column chromatography eluting with hexane. (Z)-1-(1-Nonen)-3-ynyl benzene (**4a**): Yield: 0.085 g (85%); ^{1}H NMR ($CDCl_3$) δ 7.86 (d, *J*=8.5 Hz, 2H), 7.34–7.25 (m, 3H), 6.54 (d, 11.8 Hz, 1H), 5.69 (dt, 11.8 Hz; 2.4 Hz, 1H), 2.43 (td, 7.2 Hz; 2.4 Hz, 2H), 1.60 (quint., 7.2 Hz, 2H), 1.43 (quint., 7.2 Hz, 2H), 1.34 (sext., 7.2 Hz, 2H), 0.91 (t, 7.2 Hz, 3H); ^{13}C NMR δ 137.21, 136.72, 128.43, 128.10, 128.07, 108.21, 97.84, 79.18, 31.11, 28.01, 22.20, 19.86, 13.90; LRMS *m/z* (relative intensity) 198 (25), 155 (20), 141 (100), 91 (27), 79 (12); IR (neat) cm^{-1} 3061, 3021, 2200, 1660, 1450, 784, 692; exact mass calcd for $C_{15}H_{18}$: 198.1408; found: 198.1417.

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