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Tellurium in organic synthesis: an approach to the synthesis of (*Z*,*E*)-dienic precursors of insect pheromones

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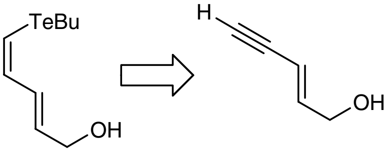
Abstract—A simple and straightforward route to (*Z*,*E*)-dienic precursors of insect pheromones was developed. The route features a cross-coupling of a (*Z*,*E*)-dienic telluride with an alkyl Lipshutz cuprate.

Several routes for the synthesis of dienic pheromones have been developed. Some of them involve a stepwise construction of the (*Z*,*E*)-dienic fragment. Others use multistep synthesis to assembly an enyne, which is then reduced to the desired (*Z*,*E*)-diene.[1,2]

Over the past years we have been concerned with the construction of unsaturated systems using tellurium chemistry.[3] One of the most useful methodologies developed by us for this purpose consists in the hydrotelluration of alkynes, leading to *Z*-vinylic tellurides.[4] Of particular interest is the tellurodiene **1**, which was already used in our group in the synthesis of a natural product.[5] The tellurodiene **1** is obtained by hydrotelluration of the commercially available and easily prepared (*E*)-pent-2-en-4-yn-1-ol **2**[6] (Scheme 1).



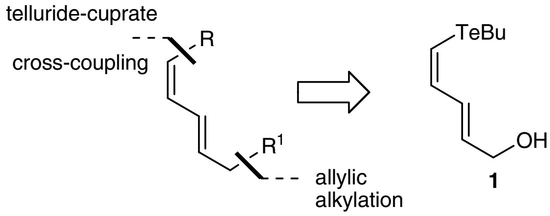
1 **2**

Scheme 1.

Keeping in mind the peculiar reactivity of vinylic tellurides,[3] specially their ability to cross-couple with cuprates,[7–10] a retrosynthetic analysis of (*Z*,*E*)-dienic pheromones shows that compound **2** could constitute a common precursor for this class of compounds (Scheme 2).

The tellurodiene **1** was prepared as described first, by hydrotelluration of **2** with a mixture of dibutylditelluride and sodium borohydride in ethanol,[11] or by reaction of **2** with lithium butyltellurolate, prepared in situ from insertion of elemental tellurium into ^{n}butyllithium in THF, in the presence of ethanol[12] (Scheme 3).

With the tellurodiene **1** in hands, it was transformed into the corresponding alcoholate **3** by reaction with sodium hydride in THF at 0 °C. After the addition of sodium hydride to the solution of **1** in THF, the mixture became brown and then turned to black. This solution was then transferred via canula to a solution of a previously prepared magnesium alkylcyanocuprate **4** in THF at room



1

Scheme 2.

$$\mathbf{1} \xleftarrow[75\%]{\text{BuTeLi, EtOH (3 eq.), THF, reflux, 6 h}} \mathbf{2} \xrightarrow[75\%]{(\text{BuTe})_2,\ \text{NaBH}_4,\ \text{EtOH, r.t., 3 h}} \mathbf{1}$$

Scheme 3.

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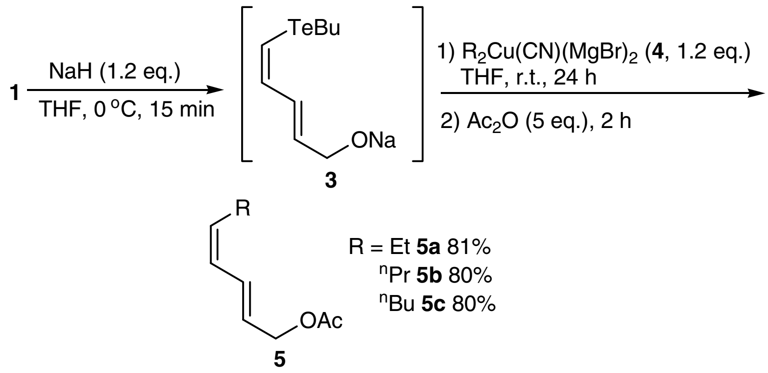
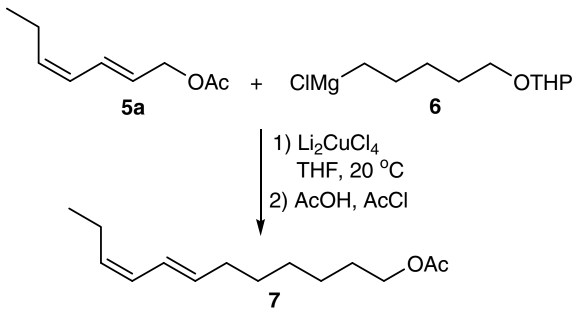


Scheme 4.



Scheme 5.

temperature and the reaction mixture was stirred at this temperature for 24 h. After this time, the mixture was treated with an excess of acetic anhydride and stirred for 2 h at room temperature. The (*Z*,*E*)-dienic acetates **5** were obtained in goods yields (Scheme 4). The acetates **5a–c** constitute precursors of the insect sex pheromones of, respectively, *Lobesia botrana*,[13] *Bombyx mori*[14] and *Malacososma disstria*.[15]

In this way, in a single operation, the telluride **1** was transformed into advanced intermediates in the synthesis of three insect sex pheromones.

Allylic acetates react with Grignard reagents under copper species catalysis.[16] In this way, treatment of the acetates **5** with the appropriate Grignard reagent in the presence of a copper catalyst would give the insect sex pheromones mentioned above. In fact, the acetate **5a** was already transformed into the sex pheromone of *Lobesia botrana* **7** by reaction with the appropriate protected Grignard reagent **6**, in the presence of dilithium tetrachlorocuprate, followed by deprotection and acetylation (Scheme 5).[13]

Further work is underway to apply this methodology in the synthesis of a whole series of pheromones containing the (*Z*,*E*)-dienic moiety[17] in their structures.

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