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LETTERS

Selectivity on the Reaction of Vinylic Tellurides with Butyllithium in the Presence of Carbonyl Compounds.

Miguel J. Dabdoub[a]*, Raquel G. Jacob[a], José T. B. Ferreira[b*†], Vânia B. Dabdoub[b] and Francisco de A. Marques[c]
[a]Laboratório de Síntese de Compostos Organocalcogênios
Departamento de Química, FFCLRP, Universidade de São Paulo, Av. Bandeirantes, 3900.
Ribeirão Preto - SP, Brasil. * E-mail: migjodab@usp.br
[b]Departamento de Química, Universidade Federal de São Carlos. São Carlos, SP - Brasil
[c]Departamento de Química, Universidade Federal do Paraná. Curitiba, Brasil

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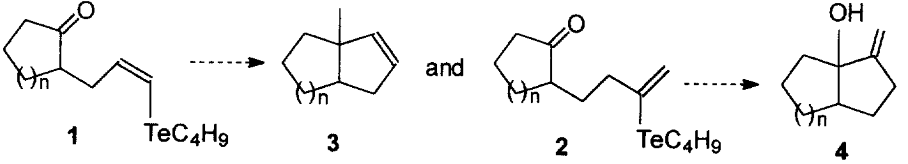
Abstract: *The treatment of isomeric vinylic tellurides 5-7 with butyllithium in THF at –78 °C in the presence of a carbonyl compound such as benzaldehyde or cyclohexanone was studied. High selectivity of the attack at the tellurium atom was observed. In most cases, the corresponding allylic alcohol was obtained as the only (or major) product instead of the alcohols derived by the 1,2 addition of BuLi at the carbonyl compound. Similar results were obtained using the ketenetelluroacetal 14 instead of the vinylic monotellurides.* © 1999 Elsevier Science Ltd. All rights reserved.

Vinylic tellurides react easily with butyllithium in THF at –78 °C to afford the corresponding vinyllithium anions with total retention of configuration.[1,2] These intermediates were subsequently trapped with aldehydes resulting in the formation of the allylic alcohols in very good yield.[2b-g] Other Te/metal exchange reactions on vinylic tellurides such as Te/Cu,[3] Te/Na,[4] Te/Mg,[4] Te/Ca[4] and Te/Zn[5] also occur with high retention of configuration of the original double bonds. Vinylmetallic intermediates are synthetically important because they are used in a variety of carbon-carbon bond forming reactions. We are interested in obtaining bicyclic systems, employing vinylic tellurides of type **1** and **2** that contain a carbonyl group in their structures. In the proposed reaction, the butyllithium first attacks the tellurium atom to provide a vinyllithium intermediate that by intramolecular reaction with the carbonyl group would be transformed into the desired bicyclic alcohols **3** and **4**.



To explore this proposal, we initially study the intermolecular competition in order to determine any differences in reactivity of vinylic tellurides and carbonyl compounds toward

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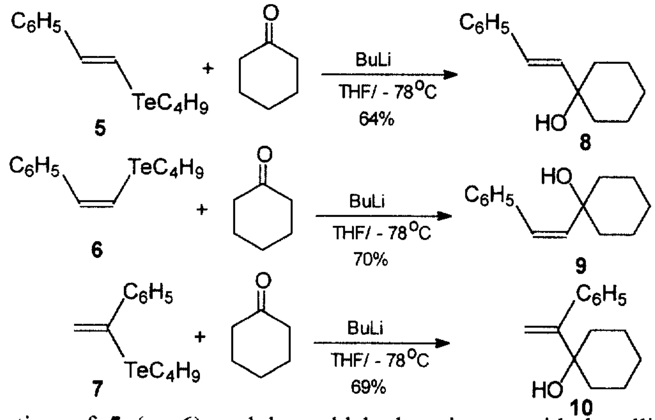
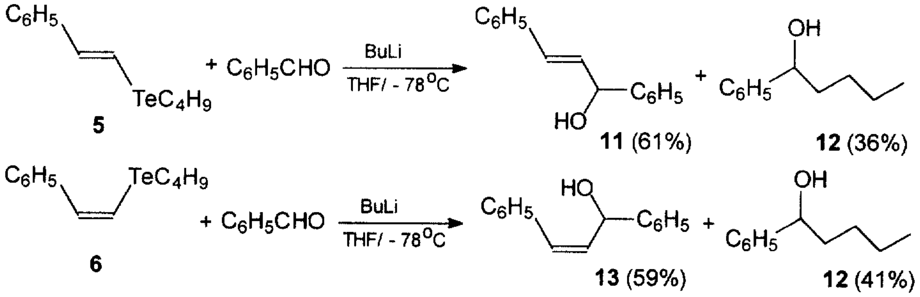
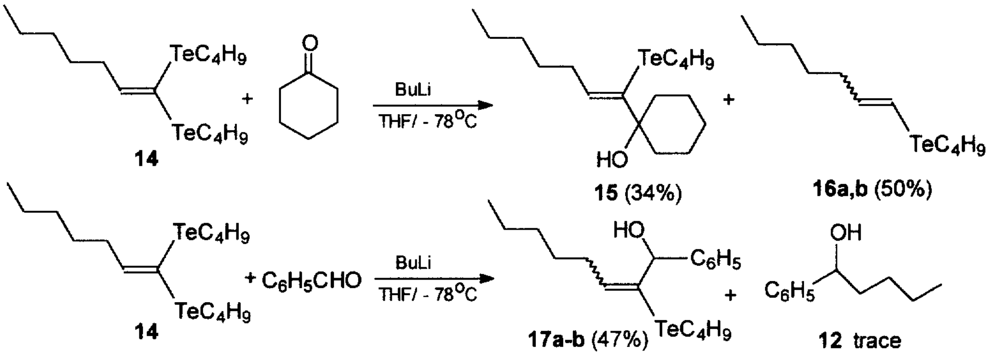
butyllithium. In addition, this study will help to elucidate the optimum condition for the intramolecular trapping experiments. In the present comunication, we describe our preliminary results concerning the significant difference of reactivity observed when a mixture of equimolar amounts of a vinylic telluride and a carbonyl compound was reacted with 1.0 equiv of butyllithium. The carbonyl compounds of choice were cyclohexanone and benzaldehyde. In all cases we observed higher reactivity of the butyltellurium over the carbonyl moiety because the corresponding allylic alcohols were always obtained as the major products.[6] The reaction of **5** with cyclohexanone results in the exclusive formation of the allylic alcohol **8** in 64% yield whereas isomer **6** reacts with the same ketone furnishing only **9** in 70% yield. Similar result was observed in the transformation of compound **7** to **10** in 69% yield. These results indicate that the Te/Li exchange initially occurs and the resulting vinyllithium anion reacts subsequently with the carbonyl compound.



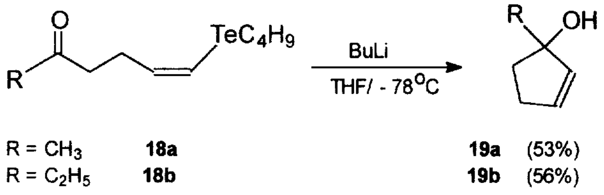
In the reaction of **5** (or **6**) and benzaldehyde mixture with butyllithium, a competition between the two reactive compounds was observed. Not only was the allylic alcohol **11** (or **13**) formed but also alcohol **12** was isolated. Even in this case, a higher reactivity of the butyltellurium moiety was observed considering that the allylic alcohols **11** and **13** were the major products (61% and 59% yield respectively). In all these cases the initial geometry of the double bonds was retained.



On the other hand, we observed that ketene telluroacetals[7] underwent the Te/Li exchange by treatment with butyllithium in THF at −78 °C leading to the formation of α-lithiated vinylic tellurides through the removal of only one butyltellurium group. The reactions of **14** and cyclohexanone or benzaldehyde with butyllithium result in the preferential formation of the corresponding allylic alcohols **15** or **17a-b**[8] (in 34% and 47% yield respectively), indicating again the higher reactivity of the butyltellurium moiety related to the carbonyl compound present in the reaction media. The lower yields of the allylic alcohols obtained **15** and **17a-b** are due to the lower reactivity of the α-lithiated vinylic telluride intermediate as compared to the vinyllithium intermediates formed from **5-7**.

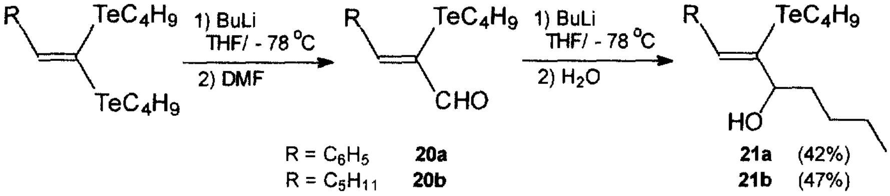


Taking advantage of the higher reactivity observed for the butyltellurium group in the presence of a carbonyl functionality toward butyllithium, we performed the desired annulation reactions employing the vinylic tellurides **18a-b** that contain a keto group in their structures. Treatment of **18a-b** in THF at −78 °C with butyllithium (in hexanes) afforded the anticipated cyclopentenols **19a-b** in 53% and 56% yield respectively.



In contrast with the results discussed above, we observed a different reaction pattern when the butyltellurium group and the carbonyl group are attached at the same carbon-carbon double bond. For instance, treatment of α-butyltelluro-α,β-unsaturated aldehydes[9] **20a-b** with 1.0

equivalent of butyllithium in THF at −78 °C showed that in this case, the carbonyl group has the highest reactivity, because the corresponding allylic alcohols **21a-b** were obtained and the butyltellurium remained intact. Further studies on the generation of vinyllithium intermediates from vinylic tellurides and the intramolecular trapping reaction with carbonyl groups to obtain bicyclic alcohols are underway in our laboratory.



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References and notes.

[†] In memory of Professor José Tércio B. Ferreira

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6. Typical procedure: To a solution of vinylic tellurium compound (2.0 mmol) and the carbonyl compound (2.0 mmol) in THF (20 mL), BuLi (2.0 mmol) was added at −78 °C under N_2. After 15 minutes, water was added (4.0 mL) and products were isolated following usual extraction procedure.[2c]
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8. Compound **17** was obtained as a mixture os *Z* and *E* isomers in a 1:1 ratio (^{1}H NMR)
9. Compounds **18a** and **18b** were prepared from the corresponding ketene telluroacetals: Dabdoub, M. J.; Jacob, R. G. *Results to be published.*