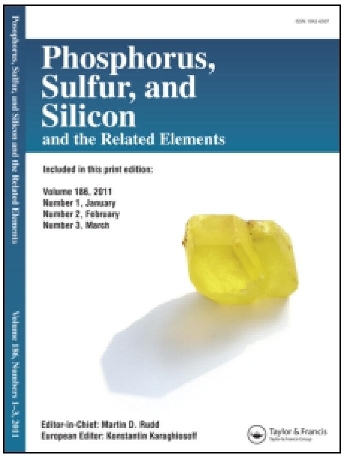

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HÉLio A. Stefani[a]; Lincoln D. G. Cardoso[a]; ClaudÉTe J. Valduga[a]; Gilson Zeni[b]
[a] Faculdade de Ciências Farmacêuticas, Universidade de São Paulo -Av., São Paulo, Brazil [b] Departamento de Química, Universidade Federal de Santa Maria, Santa Maria, RS, Brazil

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Study of the Regioselectivity in the Hydrotelluration of Hydroxy Alkynes

HÉLIO A. STEFANI[a], LINCOLN D.G. CARDOSO[a], CLAUDÉTE J. VALDUGA[a] and GILSON ZENI[b]

[a]*Faculdade de Ciências Farmacêuticas, Universidade de São Paulo -Av. Prof. Lineu Prestes, 580, 05599-970, São Paulo, Brazil and* [b]*Departamento de Química – Universidade Federal de Santa Maria – Santa Maria-RS-Brazil*

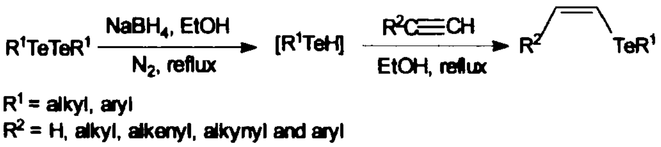
Vinylic tellurides were synthesized by the addition of organotellurols to acetylenic alcohols and the regioselectivity of the reaction was evaluated.

Keywords: tellurium; vinylic tellurides; acetylenic alcohol; hydrotelluration

1.INTRODUCTION

Alkynes have been widely used as starting materials for the preparation of vinylic selenides and tellurides and an impressive number of methodologies involving the addition of nucleophilic, electrophilic and radical species of selenium and tellurium to carbon-carbon triple bonds have been described in the literature.[1]

The addition of tellurols (or tellurolate anions) to alkynes constitutes the best known and most widely employed method to prepare vinylic tellurides.[1] Due to their exceptional propensity to oxidation, tellurols are prepared *in situ* by the reduction of the corresponding ditellurides with sodium borohydride in ethanol and immediately used in the reaction with alkynes (Scheme 1):



SCHEME 1

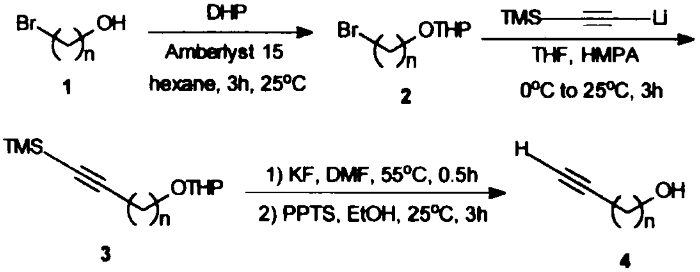
The *anti* addition of the telluride affords the *Z* stereoisomer and the tellurium moiety adds exclusively at the terminal carbon. However, when aryl-alkynes were used, the 1,1-disubstituted regioisomer was formed in minor amounts (11-28 %).

Recently, a new and efficient method for the hydrotelluration of alkynes was described.[2] It consists in the addition of *n*-butyllithium to a suspension of elemental tellurium in THF. The formation of a pale yellow solution of lithium butyl tellurolate is accompanied by the consumption of the gray tellurium powder. To this solution, the appropriate alkyne was added in deoxygenated ethanol and the mixture was refluxed.

2.RESULTS AND DISCUSSION

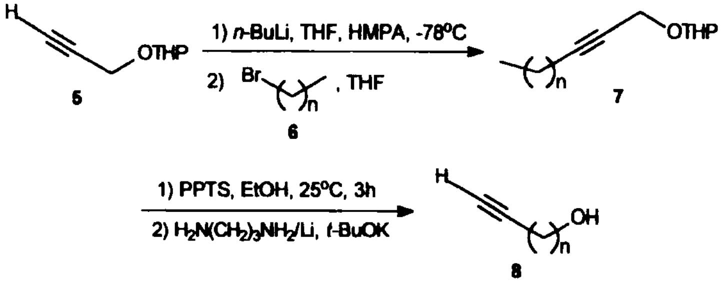
In this work we describe our studies on the regioselectivity of the hydrotelluration reaction of hydroxy alkynes with short and long chains (n = 1-9) using the methodology described above.

Protection of bromoalcohols **1** (n = 1-4) following a described procedure[3] yielded the corresponding tetrahydropyranyl ethers, **2** in 90 to 95% yield. The terminal triple bond was introduced through the reaction of **2** with the lithium anion of trimethylsilyl acetylene in THF and HMPA[4] affording the desired products in yields ranging from 65 to 90%. The trimethylsilyl group was then removed with potassium fluoride in DMF at 55°C in high yield,[5] followed by THP deprotection using PPTS in ethyl alcohol.[6] The desired hydroxy alkynes **4** were obtained in good overall yields (Scheme 2):



SCHEME 2

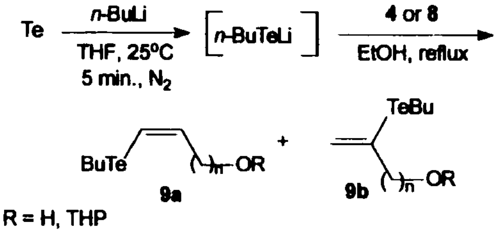
The hydroxy alkynes with n > 4 were synthesized by the reaction of the lithium anion of protected propargylic alcohol **5** with the appropriate alkyl bromide compounds **6**[4]. The yields of internal alkynes **7** were quantitative in this reaction. Deprotection, followed by prototropic transposition of the triple bond using KAPA[7] (Scheme 3) yielded the desired hydroxy alkynes **8** in good overall yields (Scheme 3).



SCHEME 3

The transposition reaction occurs smoothly and at room temperature. However, longer reaction times were required when the reaction were performed in scales up to 5.0 mmol. Interestingly the reaction did not occur with the protected alcohols.

The study of the regioselectivity in the addition of *n*-butyl tellurolate anion to the hydroxy alcohols **4** and **8** were attempted as outlined in Scheme 4.



SCHEME 4

In all cases, the stereochemistry of the vinylic tellurides **9a** was *Z*, as confirmed by NMR spectroscopy. The yields for short chains were high, but with longer chains, the yields decreased and longer reaction times were required. The ratio of the isolated products **9a** and **9b** are shown in Table 1.

TABLE 1. Ratio of isolated vinylic tellurides **9a** and **9b**.

n	**R = H**		**R = THP**	
	9a	**9b**	**9a**	**9b**
1	1.0	8.0	1.7	1.0
2	1.4	1.0	1.9	1.0
3	1.5	1.0	1.7	1.0
4	1.5	1.0	1.9	1.0
5	1.7	1.0	1.6	1.0
7	1.7	1.0	1.7	1.0
9	1.7	1.0	1.7	1.0

In order to compare the obtained results with the hydrotelluration reaction using sodium borohydride, the addition to protected and unprotected propargylic alcohol was atempted. We observed differences in the reactivity and selectivity by using the two methodologies. These differences are probably caused by an interaction between tellurium and the terminal oxygen atom in the alkyne, increasing the rate of the addition to propargylic alcohol and upon the protected alcohol. Another possibility could be the difference between the metallic cation lithium or sodium in the reaction medium. Optimization studies of this reaction are in progress in our laboratory.

ACKNOWLEDGEMENT

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