

SYNLETT Spotlight 432

Vinylic Tellurides

Compiled by Juliano Carlo Rufino Freitas



This feature focuses on a reagent chosen by a postgraduate, highlighting the uses and preparation of the reagent in current research

Juliano Carlo Rufino Freitas was born in Barreiros (Brazil) in 1985. He finished his undergraduate studies in chemistry at Universidade Federal Rural de Pernambuco in 2008 and received his M.Sc. from the Universidade Federal de Pernambuco in 2010. Currently, he is a Ph.D. student at the same university working on the development of new synthetic methods based on organometallic reactants under the supervision of Prof. Paulo Henrique Menezes. His research is focused on the synthesis of sugar derivatives and the application of organometallic compounds in natural product synthesis.

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Introduction

The ability to endure tellurium–metal exchange with retention of the double bond configuration, allowing the formation of new carbon–carbon bonds in a very selective way, makes vinylic tellurides a promising class of compounds in organic synthesis.¹

For the preparation of *Z*-vinylic tellurides,¹ the most convenient and widely used method is the hydrotelluration of alkynes. It differs from other hydrometallations in that it occurs through *anti*-addition of the tellurolate anion to the

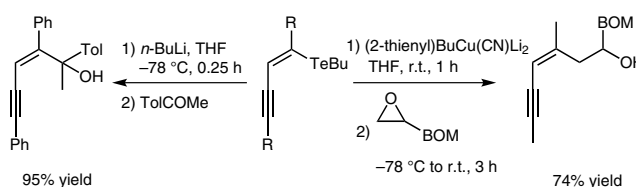
triple bond of the terminal alkyne, the regioselectivity being dependent on the nature of the alkyne source.²

Due to the simple preparation and purification procedures of vinylic tellurides compared to other organometallic reagents, the application of this class of compounds to the synthesis of biologic active compounds,³ as well as the study of their toxicological and pharmacological⁴ aspects, has experienced an exponential growth in the last years.

In addition, vinylic tellurides are air-stable and can be easily handled or stored for long periods; unlike Grignard or organolithium reagents.

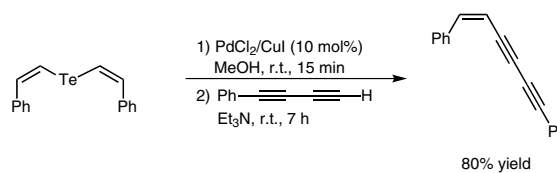
Abstracts

(A) *Tellurium–Lithium and Tellurium–Copper Exchange Reactions*
Transmetallation reactions of functionalized *Z*-vinylic tellurides can be used for the preparation of the corresponding vinyl organometallics with retention of the double bond configuration. The reaction occurs quickly at low temperatures to give the corresponding transmetallated compounds, which can further react with a variety of electrophiles (including carbonyl compounds and epoxides).⁵



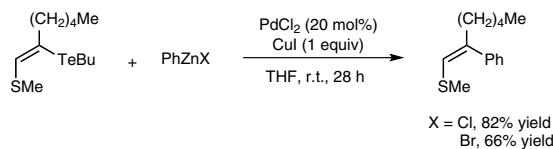
(B) *Sonogashira-type Reactions*

Vinylic tellurides can be used for the synthesis of enynes and polyacetylenes via Sonogashira-type couplings. The reactions are tolerant to a wide range of functional groups and the corresponding products are obtained in good yield under mild conditions.⁶



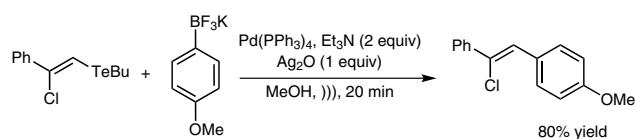
(C) *Negishi-type Reactions*

Cross-coupling reactions between functionalized vinylic tellurides and organozinc reagents in a Negishi-type coupling were also described. In the presence of palladium(II) and under mild conditions, several functionalized alkenes were obtained in moderate to good yield and high stereoselectivity.⁷



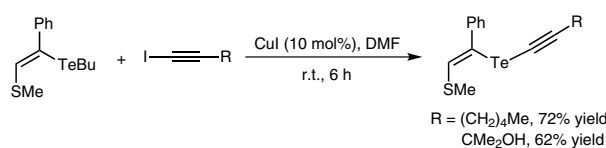
(D) Suzuki-type Reactions

The synthesis of stilbenes, 1,3-enynes and 1,3-dienes can be achieved by the use of vinylic tellurides and potassium trifluoroborate salts through a Suzuki-type cross-coupling. The desired compounds are obtained in moderate to good yield and high stereoselectivity.⁸



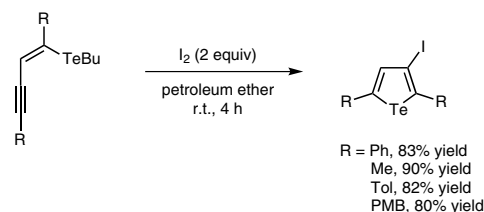
(E) Cross-Coupling Reactions using a Copper-Catalyzed System

Zeni and co-workers developed a method for the synthesis of several functionalized alkynyl tellurides from the reaction of aryl, vinyl and alkynyl tellurides with alkynyl iodides catalyzed by copper(I).⁹ The new organotellurium compounds produce antidepressive-like activity.



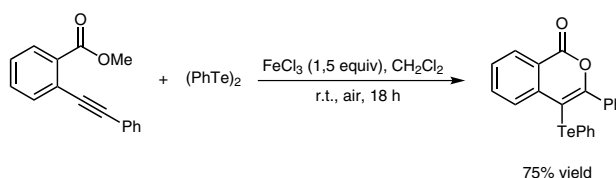
(F) Iodo-Cyclization Reactions

The first use of vinylic tellurides in electrophilic cyclization reactions was reported by Dabdoud and co-workers.^{10a} The reaction was applied to a wide variety of vinylic tellurides to give the corresponding functionalized 3-iodo tellurophenes in moderate to excellent yield.^{10b}



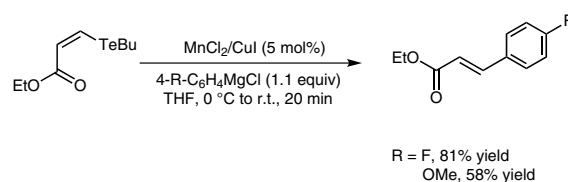
(G) Iron-Mediated Cyclizations

The synthesis of various 4-tellurium isochromenones was recently described.¹¹ The reaction occurred in the presence iron(III) under mild conditions and in air. The methodology was regioselective, providing only the six-membered ring as the product.



(H) Cross-Coupling Reactions Using a Manganese-Catalyzed System

In 2012, Comasseto and co-workers described the cross-coupling reaction between functionalized vinylic tellurides and Grignard reagents¹² using catalytic amounts of manganese(II) and copper(I). The reaction occurred quickly and several functionalized *E*-alkenes were obtained with high stereoselectivity.



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