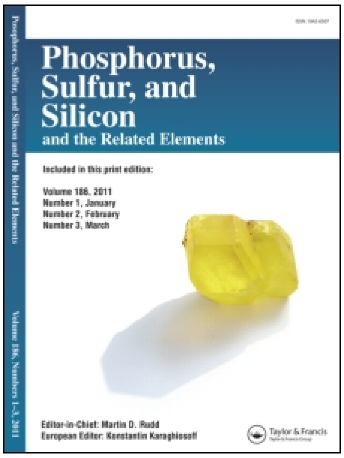

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João V. Comasseto[a]; Alcindo A. Dos Santos[b]
[a] Instituto de Química, Universidade de São Paulo, São Paulo, SP, Brazil [b] Departamento de Química, Universidade Federal de São Carlos, São Carlos, SP, Brazil

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Organotellurides as Precursors of Reactive Organometallics

João V. Comasseto[1] **and Alcindo A. Dos Santos**[2]
[1]Instituto de Química, Universidade de São Paulo, São Paulo-SP, Brazil
[2]Departamento de Química, Universidade Federal de São Carlos,
São Carlos-SP, Brazil

Reaction of organotellurides with easily available organometallics leads to a fast and clean tellurium / metal exchange reaction, allowing the preparation of a range of functionalized organometallics with C-sp$_3$, C-sp$_2$, and C-sp hybridization carbanionic centers. Some synthetic applications of the tellurium / metal exchange reactions are discussed.

Keywords Reactive organometallics; tellurium/metal exchange

INTRODUCTION

Organometallics are of fundamental importance in organic and inorganic chemistry.[1] In organic synthesis, they are one of the most usually employed classes of reagents for the carbon-carbon and carbon-heteroatom bond formation. The development of methods to prepare structurally elaborated reactive organometallics remains a field of intensive investigation.[2] The remarkable importance of organometallics is due to their capacity to act as nucleophiles and as bases also, allowing the generation of other organometallics. A fundamental query to produce a reactive organometallic reagent is related to the functional compatibility in the structure of the precursor of the organometallic reagent. Also important is the stability (inertia) of the partner produced in the reaction media during the formation of the organometallic of interest.

Among all other characteristic reactions of organotellurides, the most promising synthetic transformation of this class of compounds is their transformation into reactive organometallic compounds by reaction with commercially available alkyllithiums or with other easily

Address correspondence to Alcindo A. Dos Santos, Departamento de Química, Universidade Federal de São Carlos, CEP 13565-905, São Carlos-SP, Brazil. E-mail: alcindo@power.ufscar.br; alcindo@dq.ufscar.br

prepared organometallic species. The preparation of organic tellurium compounds is nowadays a routine practice, and compounds with defined stereochemistry can be obtained easily. Their transformation into reactive organometallics is a powerful synthetic tool that allows the formation of new carbon-carbon bonds in a stereoselective way. Considering the relative carbanion stability, an organometallic reagent attacks the tellurium atom of a diorganotelluride generating another organometallic, if the later is more stable than the former. It is worth mentioning that this is a unique property of tellurides, when compared with similar compounds of the other members of the chalcogen family. Neither sulfides nor selenides suffer such exchange reaction in a clean and mild way as the tellurides do. In the following sections, we will discuss generalities of the tellurium/metal exchange reactions and some synthetic applications of the discussed methodologies.[3]

SYNTHETIC APPLICATIONS OF TELLURIUM/LITHIUM EXCHANGE REACTIONS

The tellurium / lithium exchange is one of the fastest metalloid / lithium exchange reactions.[4] By treatment of diorganyl tellurides with alkyllithiums in THF at low temperatures, tellurium/lithium exchange occurs, generating the more stable organolithium compounds. By this procedure alkyl-, aryl-, vinyl- and alkynyllithiums, and even allyl-, and benzyllithiums can be easily obtained and trapped in situ with electrophiles.[5]

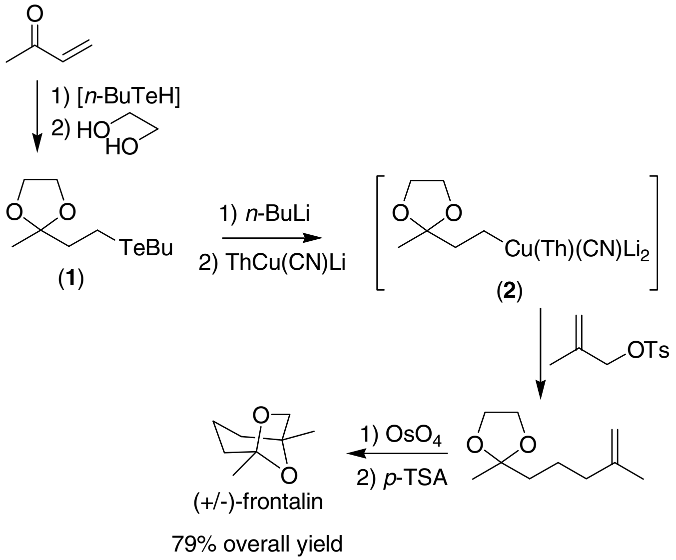
Having in mind the fact that lithium is the most electropositive metal among those with wide synthetic application (Li, Mg, Zn, Cd, Cu), the preparation of an organolithium compound formally represents the access to any other of such classes of organometallic compounds by a transmetallation reaction (Scheme 1).[2b]

$$\mathrm{R_n{-}Li} \xrightarrow{\mathrm{MX_n}} \mathrm{R_n{-}M} + (\mathrm{LiX})_n$$

$$\mathrm{M = Mg,\ Zn,\ Cd,\ Cu}$$

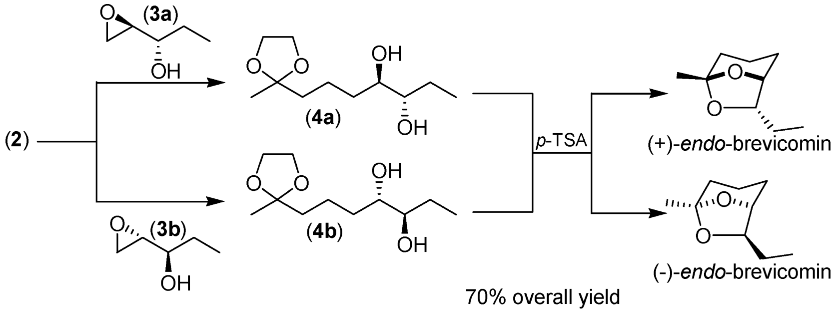
SCHEME 1

Hydrotelluration of α,β-unsaturated carbonyl compounds, produces the corresponding β-butyltellanyl carbonyl compounds that can suffer functional group interconversions.[6,7] Using the conditions presented in Scheme 4, telluride 1 was employed as a key intermediate in the synthesis of (+/−)-frontalin (Scheme 2).[8] By a similar strategy cuprate (2) was submitted to reaction with epoxides **3a** and **3b** producing the



SCHEME 2

enantioenriched diols **4a** and **4b**, precursors of (+)– and (−)-*endo* brevicomin (Scheme 3).[9]



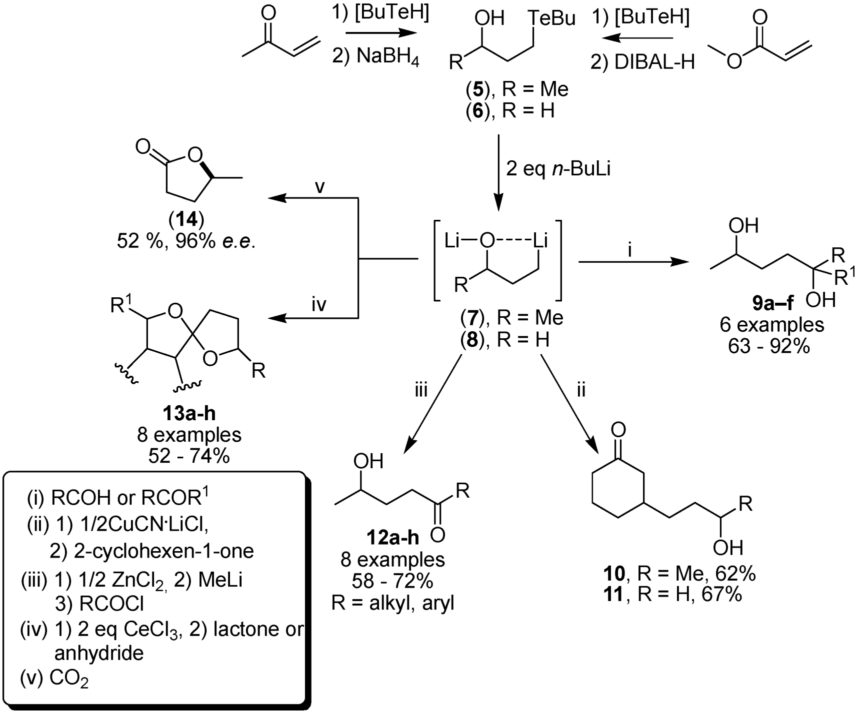
SCHEME 3

The tellanyl ketone produced by the hydrotelluration of methyl-vinyl-ketone was reduced to the hydroxyl telluride **5** by reaction with sodium borohydride. The analogue (**6**) was produced by hydrotelluration of methyl acrylate followed by reduction with DIBAL-H. Treatment of these hydroxy tellurides (**5** and **6**) with two equiv of *n*-butyllithium at −78°C produced the corresponding dianion (**7** or **8**), which reacted with aldehydes and ketones yielding diols (**9a-f**).[10] Dianions **7** and **8** reacted with CuCN·2LiCl and the pre-formed cyanocuprates added in a 1,4-manner to 2-cyclohexen-1-one yielding the hydroxy ketones **10** and **11**.[11] The dilithium salt **7** was submitted to the reaction with zinc chloride in THF solution, in different ratios. The chloro-organyl-zinc reagent did not react with carboxylic acid chlorides. The diorganyl-zinc and triorganyl-zincate presented only poor reactivity with acyl chlorides (~25%). On the other hand, the zincate generated by reaction of two equivalents of the dianion **7** with zinc chloride followed by addition of one equivalent of methyllithium, produced a reactive organometallic that reacted efficiently with alkyl and aryl acyl-chlorides in good yields.[12]

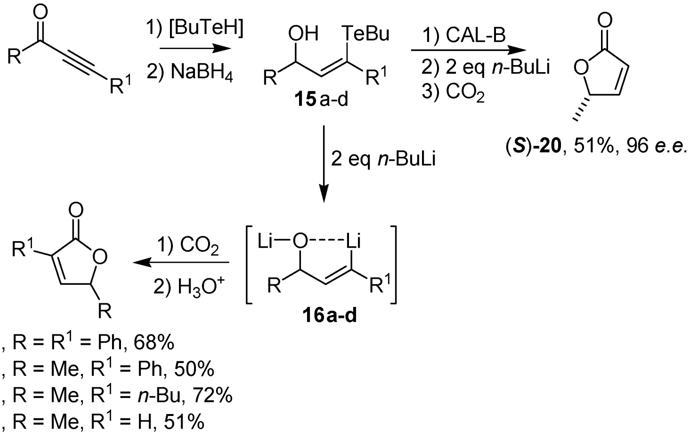
Recently it was carried out the first kinetic enzymatic resolution of hydroxy organic tellurides. The enantiomers were obtained in high optical purity (up to 99% *e.e.*) and good chemical yields. The enantioenriched isomers of the alcohol **5** were submitted to treatment with butyllithium and the (*S*)-dianion **7** was reacted with carbon dioxide leading to γ-Valerolactone (**14**).[13] Additionally, it was studied the conversion of dianions **7** and **8** into dicerium entities aiming the preparation of some spiroketals. Initially, the generated dianion (**7** or **8**) was added to a suspension of cerium trichloride in THF at low temperature and the mixture was stirred for one hour for the formation of the dicerium salt. Due to the remarkable fast reaction of hydroxy tellurides with butyllithium, it was performed an experiment where a mixture of the hydroxy telluride **5** and cerium trichloride (two equivalents) in THF was treated with two equivalents of butyllithium. TLC analysis revealed that the hydroxy telluride was totally consumed within 5 min following the addition of *n*-butyllithium. The dicerium salt was then added to the appropriate lactone or anhydride leading to spiroketals **13**.[10] In Scheme 4, the abovementioned transformations are presented.

One of the most synthetically useful reactions of organotellurides involves the addition of organotelluro nucleophiles to alkynes.[3] The products of the reaction are Z vinylic tellurides, which are precursors of *Z* vinylic organometallic reagents.

The hydrotelluration of alkynones, followed by the reduction of the carbonyl unit with sodium borohydride or DIBAL-H, lead to γ-telluro-allylic alcohols.[14] The allylic alcohol **15** and some analogues were obtained in the optical pure form by enzymatic kinetic resolution. Similarly, to **5** and **6**, the reaction of γ-telluro-allylic alcohols with two equivalents of *n*-butyllithium produced the corresponding C,O-dianion that reacted with carbon dioxide yielding bioactive butenolides (Scheme 5).[15]

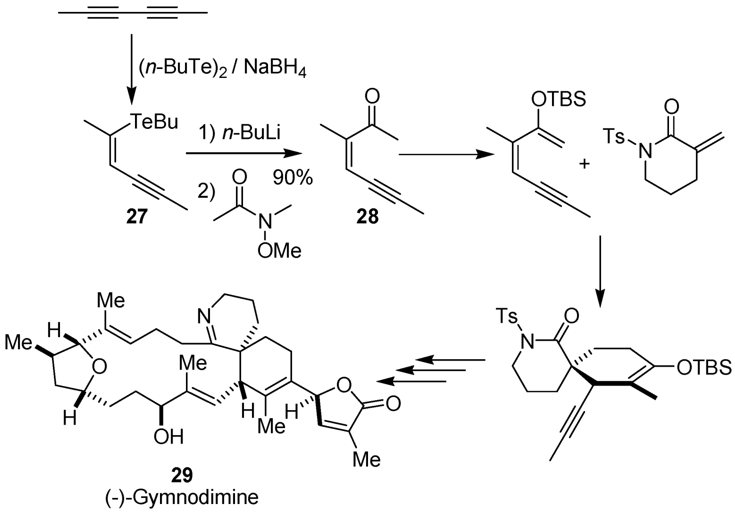


SCHEME 4



SCHEME 5

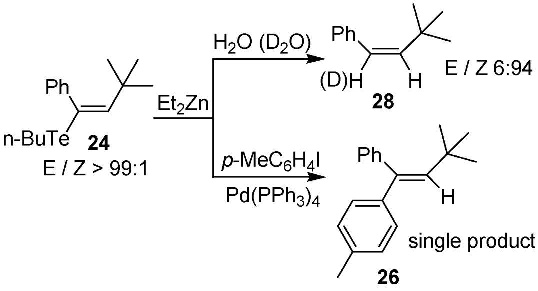
A hydrotelluration reaction, followed by a tellurium/lithium exchange (conversion of **21** into **22**), was used in the proposed total synthesis of Gymnodimine (**23**) according to Scheme 6.[16]



SCHEME 6

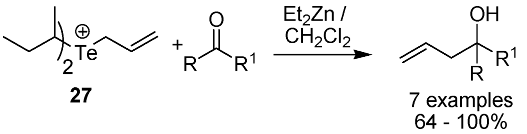
TELLURIUM/ZINC EXCHANGE REACTION

Some vinyl tellurides (e.g. **24**) react with diethyl zinc to give the corresponding vinyl zinc reagents, which are captured with H_2O or D_2O to give the detellurated olefin **25** in variable isomeric ratios. Vinyl zinc intermediates also promote palladium catalyzed coupling reactions with aryl iodide yielding substituted aryl olefins **26** (Scheme 7).[17]



SCHEME 7

Di-alkyl-allyl telluronium salts (**27**) react with diethyl zinc leading to allylic organozinc reagent, which are captured with electrophiles in excellent yields as exemplified in Scheme 8.[18,19]

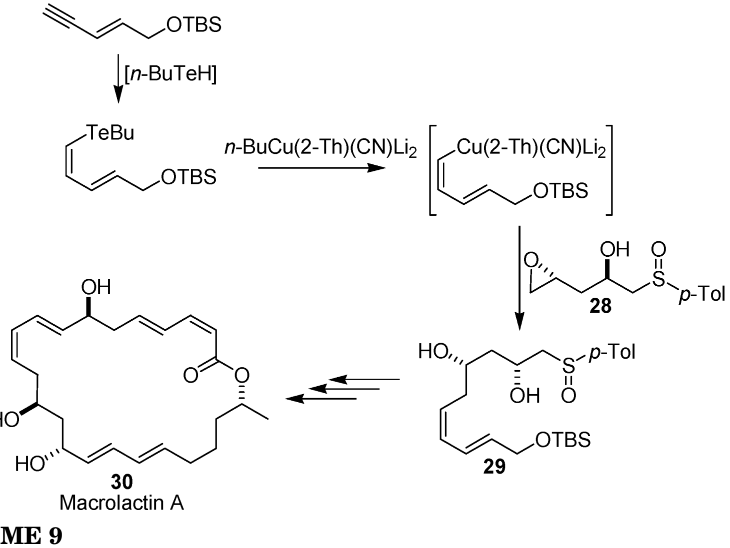


SCHEME 8

TELLURIUM/COPPER EXCHANGE REACTION

Experimental conditions to promote the tellurium/copper exchange reactions of vinyl-, allyl, and aryl-tellurides are well established.[20] The reaction with vinylic tellurides occurs with retention of the double bond geometry, and the *Z* vinyl cyanocuprates react with unhindered enones in the usual way. In THF solution and in the presence of boron trifluoride[20e] or in diethyl ether as solvent in the absence of Lewis acids even hindered enones react successfully.

The *Z* vinylic cyanocuprates also react with epoxides (e.g. **28**), giving the *Z* homoallylic alcohols (e.g. **29**).[20a,20h] The reaction is stereospecific and this transformation was used in a key of a total synthesis of Macrolactin A (**30**) (Scheme 9).[21]



SCHEME 9

FINAL CONSIDERATIONS

In the last two decades, the organic chemistry of tellurium experienced a great development and nowadays many practical methods to introduce and to remove tellurium into and from organic substrates are available. The experience gained by the chemists dedicated to this branch of the chemistry shows that many negative comments found in the old literature, concerning the instability and the bad smell of the organotellurium compounds, cannot be considered a rule. Further, they found that these compounds can be prepared and manipulated safely in a conventional organic synthesis laboratory, which was demonstrated by the synthetic transformations presented in this account.

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