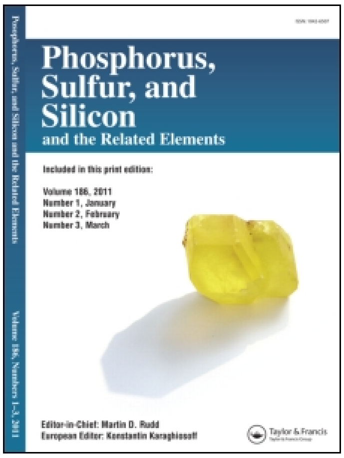

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New Aspects of Old Reactions in Organotellurium Chemistry

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NEW ASPECTS OF OLD REACTIONS IN ORGANOTELLURIUM CHEMISTRY

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Abstract: The more general methods to prepare nucleophilic and electrophilic species of tellurium and their reaction with organic substrates are reviewed. Some detelluration reactions of organic derivatives of tellurium with possible utility in organic synthesis are discussed.

INTRODUCTION

Although the first organotellurium compound was prepared in 1840[1] this branch of organic chemistry had not been systematically studied until the middle of the present century. The first serious attempt to systematize the organotellurium chemistry was undertaken by Rheinboldt, a german chemist who introduced chemistry in Brazil in 1934, working in the then recently founded São Paulo University. Rheinboldt and his coworkers reinvestigated several described reactions of tellurium and inorganic compounds of this element with organic substrates as well as the reactivity of the resulting organotellurium compounds. The knowledge available until the middle of the 1950's in this field of organic chemistry was critically reviewed by Rheinboldt in 1954[2]. By the end of the 1950's Petragnani, the last doctoral student directed by Rheinboldt, initiated a systematic study of the interaction between organotellurium reagents and organic substrates. Petragnani's original work constitutes the basis for most of the present investigations whose aim is the use of tellurium reagents for synthetic purposes[3].

In the last ten years a considerable developement of organic tellurium chemistry has been observed and several review articles and books on the subject have been published[4-12]. This article does not intend to be a review but rather an attempt to give a brief and comprehensive view of synthetic organic tellurium chemistry, focusing attention upon the more general reactions used to prepare organotellurium compounds and the useful synthetic transformations promoted or suffered by them. Emphasis will be given to the recent contributions of our laboratory where we explore old reactions trying to establish their generality or making transformations into organotellurium compounds which can lead to useful synthetic methodologies.

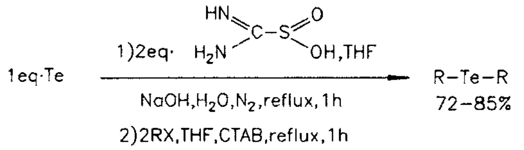
1. GENERATION OF NUCLEOPHILIC TELLURIUM SPECIES

The main sources of nucleophilic tellurium species are elemental tellurium and diorganylditellurides.

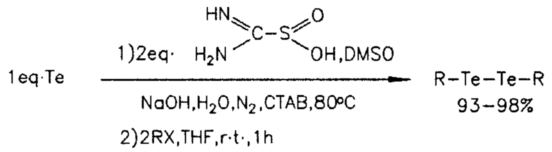
(A) Reaction of Elemental Tellurium with Reducing Agents.

Elemental tellurium reacts with a number of reducing agents to give nucleophilic tellurium species such as alkaline hydrogentellurides and alkaline tellurides or ditellurides. The nature of the product can vary depending on the tellurium/reducing agent ratio, on the reaction conditions and on the nature of the reducing agent. The methods to generate such species were recently reviewed by us[12].

A new method to generate sodium telluride or ditelluride was developed in our laboratory. Reaction of formamidinesulfinic acid (thioureadioxide, TUDO) in alkaline medium with elemental tellurium leads to sodium telluride or ditelluride which react with alkyl halides to give the corresponding dialkyltellurides and ditellurides (Eqs. 1, 2)[13].



Eq.1



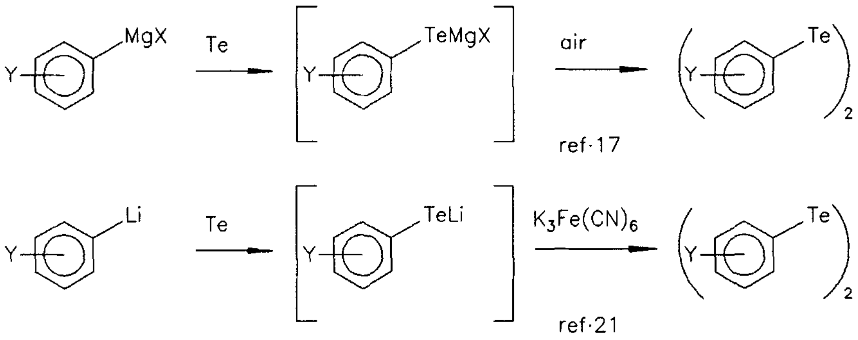
Eq.2

All the above mentioned nucleophilic tellurium species are air sensitive and must be generated in a carefully deoxygenated inert atmosphere, being used in situ for further reactions.

(B) Reaction of Elemental Tellurium with Grignard Reagents and Organolithiums.

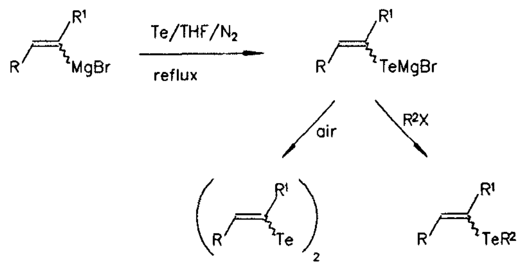
The reaction of elemental tellurium with alkyllithiums and alkyl Grignard reagents was not extensively studied[14,15]. The reaction of elemental tellurium with aryl Grignard reagents was investigated in more detail[4,16]. When the reaction is performed in THF in the presence of small amounts of oxigen, the product obtained after air oxidation of the reaction mixture is the corresponding diarylditelluride[17]. The insertion of elemental tellurium into a carbon-lithium bond occurs more easily[18-20]. Recently the synthesis of a number of diarylditellurides by means of the reaction between aryllithiums and elemental tellurium followed by oxidation was described[21].

Scheme 1



The reaction of elemental tellurium with vinylmagnesium bromide in THF was explored by us as a route to prepare magnesium vinyltellurolates, precursors of vinylic tellurides and vinylic ditellurides[22,23] (Scheme 2).

Scheme 2



The ease of the insertion reaction depends on the tellurium used. When coarse-grained tellurium is used, the element does not dissolve even under reflux; 150-300 mesh tellurium reacts only by heating the mixture under reflux, and fine-grained tellurium (300 mesh) reacts spontaneously and with heat evolution. In all cases the elemental tellurium was heated for 12 hs at 110°C prior to the addition to the Grignard solutions. To obtain divinylditellurides it is essential to oxidize the mixture with air prior to the addition of any proton source to the reaction mixture. If water or ammonium chloride is added prior to the oxidation step, a complex mixture of products is obtained.

The insertion of elemental tellurium into sp carbon-metal bonds is much easier and was explored by several authors in the preparation of metal acetylenic tellurolates (Eq.3)[24,25].

$$R-\equiv-M \xrightarrow{Te^{0}} R-\equiv-TeM \qquad \text{Eq.3}$$

$$M = MgX,\ Li,\ Na$$

The method used in our laboratory consists of the generation of lithium acetylides by reacting the corresponding acetylene with n-butyllithium in THF at 0°C under nitrogen, followed by addition of elemental tellurium (mesh 200-300) previously dried for 12 h at 110°C, heating the mixture under reflux for about 30 min until the element is completely dissolved[25].

(C) Transformation of Diorganylditellurides into Organotellurolate Anions

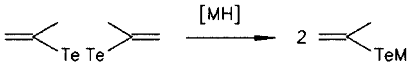
The reduction of the tellurium-tellurium bond of diorganoditellurides by sodium borohydride in ethanol, introduced by Piette and Renson[18] is the method of choice to generate organotellurolate anions[5,12]. Lithium aluminium hydride has also been employed to reduce diorganylditellurides to lithium organyltellurolates[26]. Other methods to generate such species are available, e.g., the reaction of diorganylditellurides with sodium and potassium in liquid ammonia[27] or lithium in THF[28].

$$\mathrm{RTeTeR} \xrightarrow{[\mathrm{MH}]} 2[\mathrm{RTeM}] \qquad \text{Eq.4}$$

$[\mathrm{MH}] = \mathrm{NaBH_4}$ [17]; $\mathrm{LiAlH_4}$ [26]; $\mathrm{Na,K/NH_3}$ [27]; Li/THF[28].

In our laboratory we generated organyltellurolate anions by reaction of diorganylditellurides with aqueous sodium hydroxide in analogy with the long known similar disproportionation reaction of diorganyldisulfides[29] and diorganyldiselenides[30]. In our work we employed a two phase system using an ammonium salt as catalyst. The sodium organyltellurolate was captured by an alkyl halide leading to diorganyltellurides[31]. The yields are improved by adding to the reaction mixture formamidinesulfinic acid (thioureadioxide)[32] which probably reduces the by product of the disproportionation reaction (sodium aryltellurinate) to the corresponding tellurolate anion[33].

The above mentioned method to reduce tellurium-tellurium bonds was employed by us to reduce divinylditellurides (see section 1.B) to the corresponding vinyltellurolate anions (Eq.5)[23], which can be captured by electrophiles (see section 3B, C, D).



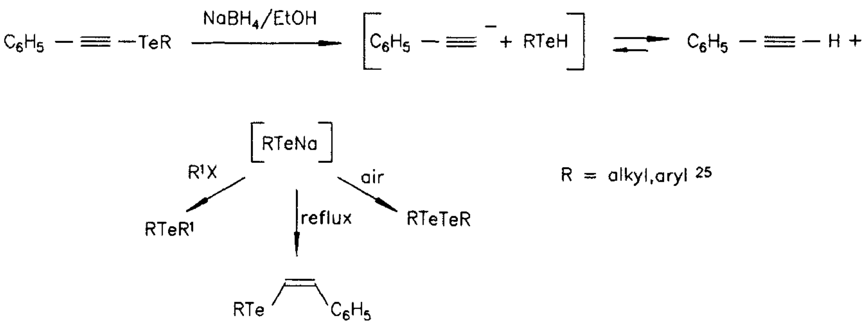
Eq.5

$[\mathrm{MH}] = \mathrm{NaBH_4,NaOH/EtOH}$,reflux; TUDO,NaOH,PTC,r. t.;
$\mathrm{Li/NH_3}$,−78°C; $\mathrm{LiAlH_4}$,r. t.

It must be emphasized that the presence of NaOH in the reaction medium during the reduction of divinylditellurides with sodium borohydride is crucial. In the absence of sodium hydroxide, the product obtained after air oxidation of the reaction mixture is the corresponding dialkylditelluride[23].

Another method to generate organyltellurolates developed by us is the reduction of carbon-tellurium bonds of acetylenic tellurides with sodium borohydride in ethanol[25]. Depending on the reaction conditions, diferent products can be obtained (Scheme 3).

Scheme 3

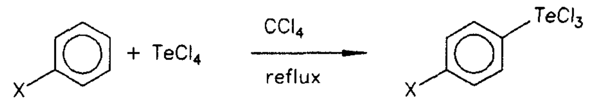


2. GENERATION OF ELECTROPHILIC TELLURIUM SPECIES

The main sources of electrophilic tellurium species are tellurium tetrachloride, tellurium dioxide and diorganylditellurides.

(A) Reaction of Tellurium Tetrachloride with Unsaturated and Organomercuric Compounds

The reaction of tellurium tetrachloride with aromatic compounds containing an electron donating substituent leads to organotellurium trichlorides[4,5,34,35]. Unactivated aromatic compounds only react with tellurium tetrachloride in the presence of a Lewis acid ($AlCl3$)[36,37]. However, the reaction is dificult to control and a mixture of products is often obtained. This problem is circunvented by reacting tellurium tetrachloride with arylmercuric chlorides, to obtain aryltellurium trichlorides with non activating substituents in the aromatic ring[4,34]. Acetylenes react with tellurium tetrachloride leading to the corresponding vinylic tellurium trichlorides[38,39]. Addition of tellurium tetrachloride to olefins was described several years ago by Petragnani[40]. Recently the reaction was reinvestigated by Engman[41,42].Tellurium tetrachloride reacts with ketones (probably via the enol form) to give the corresponding α-trichlorotellurium ketones[43]. Among the above mentioned reactions only the reaction of tellurium tetrachloride with activated aromatic compounds[4,5,34,35] and with arylmercuric chlorides[4,34], leading to aryltellurium trichlorides (Eqs.6,7) have a general character and find large use in the synthesis of organic derivatives of tellurium. It is worth mentioning that the reduction of this class of organic tellurium compounds is one of the more efficient methods used to prepare diorganylditellurides (Eq.8)[3-5].



Eq.6

Eq.7

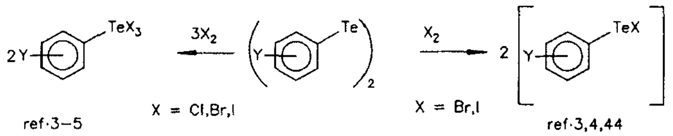
$$RTeCl_3 \xrightarrow{[H]} RTeTeR \qquad \text{Eq.8}$$

$[H] = K_2S_2O_5, Na_2S.9H_2O, H_2NNH_2.H_2O$ [4], $H_2NC(=NH)SO_2H$[33].

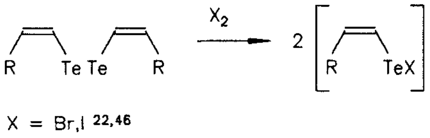
(B) Cleavage of Tellurium-Tellurium Bonds of Diorganylditellurides with Halogens.

Treatment of diorganylditellurides with stoichiometric amounts of chlorine, bromine or iodine leads to the corresponding organyltellurium trihalides (Scheme 4)[3-5]. Treatment of diorganylditellurides with equimolar amounts of bromine or iodine gives the corresponding organyltellurenyl halides[3,4,44]. Most derivatives of this class of tellurium compounds are stable only in solution and are used in situ for further reactions. Some examples of stable organyltellurenyl halides are known[4,45].

Scheme 4



In our laboratory divinylditellurides (see section 1.B) were transformed into vinyltellurenyl iodides by reaction with equimolar amounts of iodine[22]. Worthy of note is the fact that the reaction of divinylditellurides with bromine also leads to vinyltellurenyl bromides, with no addition products to the double bond being observed (Eq.9)[46]. The vinyltellurenyl halides can be captured by electrophiles (see section 4.A).

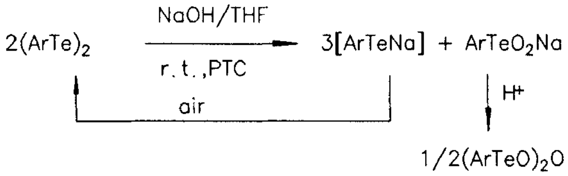


Eq.9

(C) Hydrolysis of Aryltellurium Trichlorides and Diarylditellurides to Aryltellurinic Anhydrides

Aryltellurinic anhydrides, which found use in organic synthesis as oxydizing and cyclization[47] agents can be prepared by reaction of aryltellurium trihalides with sodium hydroxide as described by Petragnani[48]. Alternativelly these reagents can be obtained by reaction of diarylditellurides with sodium hydroxide at room temperature in the presence of air in a two phase system using an ammonium salt as catalyst[31]. By reaction with sodium hydroxide the diarylditelluride disproportionates to give sodium aryltellurinate and sodium aryltellurolate (see section 1.C) which by air oxidation regenerates the diarylditelluride. The process is repeated until transformation of the diorganylditelluride to the sodium aryltellurinate is complete. Acidification of the reaction medium gives the aryltellurinic anhydride (Scheme 5).

Scheme 5



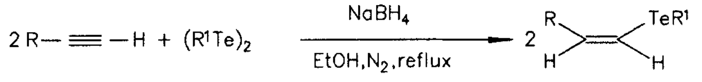
3. INTERACTION OF NUCLEOPHILIC TELLURIUM SPECIES WITH ORGANIC SUBSTRATES

(A) Reduction of Organic Substrates

The first example of the reduction of an organic substrate by a tellurium reagent was provided by Petragnani, who transformed vic-dihalides into olefines by means of a diaryltelluride[49]. Barton and coworkers[50] used this reaction in a catalytic oxidative process, which used 1,2-dibromotetrachloroetane to regenerate the oxidation agents diaryltelluroxide. Variation of these dehalogenation reactions employing tellurolate anions were reported in recent years. Presently many other functionalities can be reduced by reaction with several nucleophilic tellurium reagents. These reactions are at present the most useful synthetic transformations involving tellurium reagents and were recently reviewed by us[12].

(B) Addition of Tellurolate Anions to Acetylenes

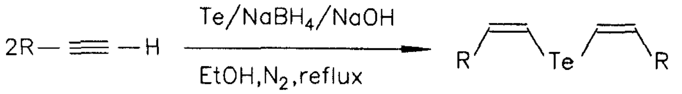
The additions of aryltellurolate anions to acetylenes has been described by several authors (Eq.10)[22,50-55]. The reaction seems to be a **trans** stereospecific addition, since the only product observed is the corresponding **cis** vinylic telluride[56]. We observed that the reaction is faster with alkyltellurolate anions than with aryltellurolates. The process presents a high regioselectivity with aromatic and conjugated acetylenes. With acetylenes bearing electron atracting groups at the carbon 3 the regiochemistry is still high leading to the **cis** olefin with the tellurium atom at the terminal carbon atom of the double bond as the main product. Aliphatic acetylenes give low yields and mixture of the two possible regioisomers[51].



Eq.10

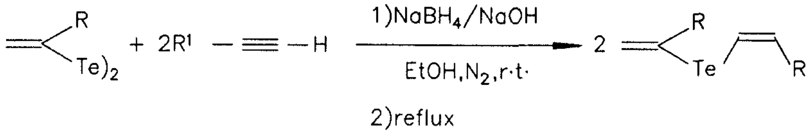
R^1 = alkyl,aryl

Reaction of acetylenes with sodium telluride, generated by reducing elemental tellurium with sodium borohydride in the presence of sodium hydroxide in ethanol/water under reflux in a carefully deoxygenated inert atmosphere, leads to divinyl tellurides. The reaction is also a **trans** addition giving the **cis** divinyl tellurides (Eq.11)[51].



Eq.11

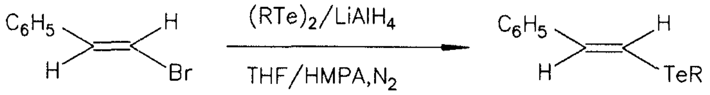
As mentioned before (section 1.C) divinyl ditellurides are reduced to the corresponding sodium vinyltellurolates by reaction with sodium borohydride/sodium hydroxide[23]. Addition of these intermediates to an acetylene gives nonsymmetrical divinyl tellurides (Eq.12)[51].



Eq.12

(C) Vinylic Substitution of Vinylic Halides by Organyltellurolate Anions

Reaction of lithium p-methoxyphenyltellurolate and lithium butyltellurolate (generated by reduction of the corresponding diorganylditelluride with lithium aluminium hydride), with **trans**, *β*-bromo-styrene in THF/HMPA, gives the corresponding vinylic telluride of **trans** configuration. The alkyltellurolate reacts faster than the aromatic one (Eq. 13)[22].



Eq.13

Alternativelly the organyl tellurolate anion can be generated by reduction of the diorganyltelluride with sodium in HMPA.

(D) Reaction of Organotellurolate Anions with Haloacetylenes

Lithium alkyl- and alkynyltellurolates generated as described in section 1.B react with 1-bromo-2-phenyl ethyne to give the corresponding acetylenic tellurides.[57]

$$R{-}TeLi + C_6H_5{-}{\equiv}{-}Br \longrightarrow C_6H_5{-}{\equiv}{-}TeR$$

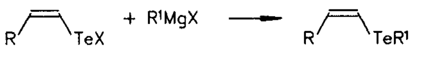
Eq.14

R = alkyl,alkynyl

4. INTERACTION OF ELECTROPHILIC TELLURIUM SPECIES WITH ORGANIC SUBSTRATES

(a)Reaction with Grignard Reagents

The reaction of aryltellurenyl halides with Grignard reagents leading to diorganyltellurides was described several years ago[44]. Recently we used this reaction to prepare vinylic tellurides and bis vinyltellurides by reacting vinyltellurenyl halides (see section 2.B) with vinyl Grignard reagent (Eq.15).



X = BrI; R^1 = alkyl,vinyl,aryl

Eq.15

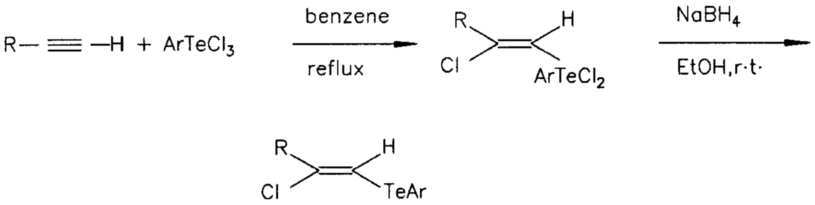
The tellurium atom of acetylenic tellurides presents electrophilic character, reacting with organolithiums or Grignard reagents to give a tellurium free acetylene and diorganyltellurides. In this way acetylenic tellurides can be considered tellurenyl acetylides[21].

$$C_6H_5-\equiv-TeR \xrightarrow[2)\,H_2O]{1)\,2R^1MgX\ \text{or}\ R^1Li} C_6H_5-\equiv-H + R^1TeR$$

Eq.16

(B) Reaction with Acetylenes

The reaction of aryltellurium trichlorides with acetylenes was recently investigated in our laboratory[58]. It was observed that the addition occurs in a *syn* fashion leading to a Z arylvinyltellurium dichloride as demonstrated by X-ray diffraction of one derivative[59]. The dichlorides are reduced to the corresponding tellurides by reaction with sodium borohydride in ethanol (Eq.17)[58].



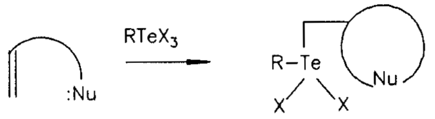
Eq.17

(C) Reaction with Olefins Containing an Internal Nucleophile

The reaction of electrophilic species with olefines containing an internal nucleophile (cyclofunctionalization) is a powerfull tool in organic synthesis[60]. One of the most important of such reactions is selenocyclofunctionalization, described for the first time by Petragnani in 1959[61]. A similar transformation involving tellurium reagents was reported in the same paper[61], but did not receive the same attention as did the selenocyclofunctionalization.

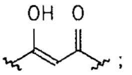
Aryltellurium trichlorides[61-63], tellurium dioxide/lithium chloride in acetic acid[64,65] and aryltellurinic anhydride[47,66,67] have been used to perform the cyclofunctionalization of unsaturated carboxylic acids[61,62], alcohols[47,63-67], carbamates[47,67], β-dicarbonylcompounds[68] and benzylethers[69] (Scheme 6).

Scheme 6



Nu = CO_2H; $RTeX_3$ = $ArTeCl_3$[61,62]

OH; $ArTeCl_3$[63], $TeO_2/LiCl/ACOH$ [64,65], $(ArTeO)_2O$ [47,66]



; $ArTeCl_3$ [68]

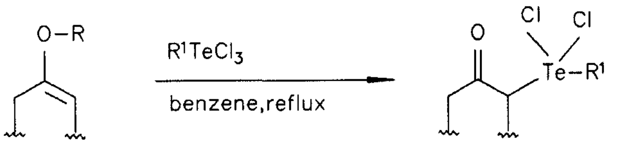
OR; $ArTeCl_3$ [69]

$NHCO_2Et$; $(ArTeO)_2O$ [47,67]

Several transformations such as telluroxide elimination[66], bromodetelluration[66], reduction[70] and reductive akylations[70] can be effected on the cyclic products, demonstrating the synthetic potential of the reactions.

(D) Reaction with Ketones and Ketone Silyl Enol Ethers

Aryl- and alkyltellurium trichlorides react with ketones[71-75] and ketone silyl enol ether[74,75] to give the corresponding α-dichloro(organyltelluro) ketones. The ketones probably react via the enol form (eq.18).



Eq.18

R = H; Me$_3$Si ref·72,75

R^1 = p–CH$_3$OC$_6$H$_5$

The reaction with ketonesilylenol ethers is faster and gives higher yields than the reaction with ketones[75].

5. DETELLURATION OF ORGANOTELLURIUM COMPOUNDS

The functional transformations promoted by tellurium reagents are synthetically valuable only if mild and selective methods to remove tellurium from the organic products are available. The tellurium atom can be removed from organic substrates by telluroxide elimination, by reduction of tellurium carbon bonds, by transmetallation with organolithium or with higher order cyanocuprates and by reaction with halogens.

(A) Oxidative Removal of Tellurium from Organic Substrates

The oxidative removal of tellurium from organic substrates has been performed by several methods, e.g., oxidation of tellurides followed by **syn** elimination[5,76], transformation of tellurides into telluroxides by bromination followed by reaction with aqueous sodium hydroxide and subsequent elimination[77], reaction of tellurides with chloroamine T followed by elimination[5,78], oxidation of benzyl and allyltellurides by air[31] or by hydrogen peroxide, t-butyl hydroperoxide, and sodium periodate[79] followed by spontaneous decomposition of the telluroxide to give oxigenated products. However none of these methods compete with analogous transformations involving selenium reagents and the oxidative removal of tellurium from organic substrates seems to be to date devoid of practical interest[5,12].

(B) Reductive Removal of Tellurium from Organic Substrates.

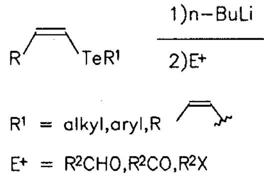
Diorganyltellurides and diorganyltellurium dichlorides can be reductively detellurated by reaction with triphenyl[64,80] or tributyltin hydrides[62,70]. The reaction occurs through a free radical intermediate, although no radical initiator is necessary. The intermediate free radical can be captured with acrylates leading to chain elongation products[70]. It must be emphazised that this reduction method is selective, being compatible with the presence of other functionalities.

Other reagents such as Raney Nickel and copper powder were also used to promote the detelluration of organic tellurides. However, we feel that more selective and practical methods to promote reductive detelluration of organic substracts are lacking and much work has to be done in this particular area.

(C) Transmetallation with Organolithiums

The lithium-tellurium exchange is a long known reaction[81-85]. However, only recently this reaction has been extensively explored for synthetic purposes. In this way alkyl-[87,91,92], carbamoyl-[88] benzyl-[87], aryl-[87], vinyl-[87,89], acyl-[90], and ethynyllithiums[87] were prepared by means of the reaction of the corresponding organotellurium compounds with butyllithium.

Recently we studied the transmetallation reaction between vinylic tellurides and butyllithium[89]. We found that the reaction is general and occurs with retention of the olefin geometry. The vinyllithiums were trapped with electrophiles, such as aldehydes, ketones and alkyl halides (Eq.19).



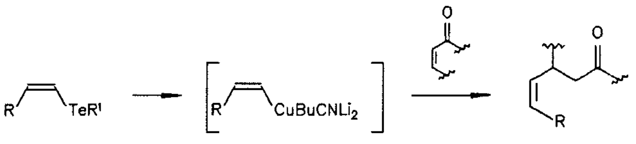
Eq.19

When R^1 is an aryl group the transmetallation can lead to a vinyl- or to an aryllithium and normally a mixture of products is obtained after capture with the electrophile. In this way, an alkyl group R^1 is required to generate only the desired vinyllithium. When R^1 is a vinyl group, two equivalents of the vinyllithium are formed for each equivalent of the starting vinylic telluride.

(D) Transmetallation with Higher Order Cyanocuprates

A novel reaction involving vinylic tellurides was developed in our laboratory. The reaction of vinylic tellurides with higher order cyanocuprates gives the corresponding vinylcuprates with retention of the olefin geometry[93]. The vinylic cuprates react with enones to give the 1,4-addition products (Scheme 7).

Scheme 7



(E) Halodetelluration

The replacement of the tellurium atom of benzyltellurides by a halogen is a long known reaction[94]. In recent times the halodetelluration of organyltellurides, diorganyltellurium dihalides and organyltellurium trihalides has been effected by photolysis[5,95], thermolysis[5,96] and by reaction with halogenating agents[5,39,97-99]. In our laboratory we transformed α-dichloro(organyltelluro) ketones into α-telluroketones by thermolysis[74] or by reaction with halogens[75]. Halogenolysis of telluroacetylenes afforded 1,1,2-trihaloalkenes via an intermediate halocetylene (Eq.20)[100].

$$R-C\equiv C-TeR^1 \xrightarrow[r.t.,-R^1TeX_3]{2X_2} R-C\equiv C-X \xrightarrow{X_2} RC(X)=CX_2 \qquad \text{Eq.20}$$

X = Br, I

CONCLUSION

From an obscure branch of the organic chemistry, the organotellurium chemistry has emerged in recent years as a promissing and advantageous alternative for some important synthetic operations. As can be anticipated the developement of some reactions commented in this article discloses new perspectives for the preparative organotellurium chemistry as well as for challenging synthetic applications.

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REFERENCES

1. F.Wöhler, Liebigs Annalen der Chemic, **35**, 111(1840).
2. H. Rheinboldt, Houben Weyl, "Methoden der Organischen Chemie", Georg Thieme Verlag, Stuttgart, 1955, vol.9.
3. K.J. Irgolic, "The Organic Chemistry of Tellurium", Gordon and Breach, New York, 1974.
4. N. Petragnani and J.V. Comasseto, Proceedings of the Fourth International Conference on the Organic Chemistry of Selenium and Tellurium, Berry, F.J., McWinnie, W.R., Eds, The University of Aston in Birmingham, 1983, p.98-241.
5. N. Petragnani and J.V. Comasseto, Synthesis, 1(1986).
6. L. Engman, Acc.Chem.Res., **18**, 274(1985).
7. L. Engman, Phosphorus and Sulfur, **38**, 105(1988).
8. S. Uemura, J. Synth. Org. Chem. Jpn., **41**, 804(1983).
9. H. Suzuki, J. Synth. Org. Chem. Jpn., 603(1987).
10. I.D. Sadekov, B.B. Rivkin, V.I. Minkin, Russian Chem. Rev., **56**, 343(1987).
11. "The Chemistry of Organic Selenium and Tellurium Compounds", Patai, S. ed., John Wiley, Chinchester, 1986, vol.1; 1987, vol.2.
12. N. Petragnani and J.V. Comasseto, Synthesis, 000(1991).
13. J.T.B. Ferreira, A.R.M. de Oliveira and J.V. Comasseto, Synth. Commun., **19**, 239(1989).
14. C.H.W. Jones and R.D. Sharma, J. Organomet. Chem., **61**, 255(1983).
15. M.P. Cava and L. Engman, Synth. Commun., **12**, 163(1982).
16. N. Petragnani and M.M. Campos, Chem. Ber., **96**, 249(1963).
17. W.S. Haller and K.J. Irgolic, J. Organometal. Chem., **38**, 97(1972).
18. J.L. Piette and M. Reuson, Bull. Soc. Chim. Belg., **79**, 353 (1970).
19. N. Deren, J.L. Piette, J. Van Coppenolle and M. Renson, J. Heterocycl. Chem., **12**, 423(1975).
20. D. Seebach and A.K. Beck, Chem. Ber., **108**, 314(1975).
21. L. Engman and J. Persson, J. Organomet. Chem., **388**, 71(1990).
22. M.J. Dabdoub, V. Dabdoub, J.V. Comasseto and N. Petragnani, J. Organomet. Chem., **308**, 211(1986).
23. M.J. Dabdoub and J.V. Comasseto, J. Organomet. Chem., **344**, 167(1988).
24. L. Brandsma and H. Verkruijse "Preparative Polar Organometallic Chemistry 1" Springer-Verlag, Berlin, 1987.
25. M.J. Dabdoub and J.V. Comasseto, Organometallics, **7**, 84(1988).
26. N.V. Kondratenko, V.I. Popov, A.A. Kolomeitsev, I.D. Sadekov, V.I. Minkin and L.M. Yagupol'skü, J. Org. Chem. USSR, **15**, 1394(1979).
27. J. Liesk, P. Schultz, G. Klar, Z. Anorg. Allg. Chem., **435**, 98(1977).
28. K.J. Irgolic, P.J. Busse and R.A. Grigsby, J. Organomet. Chem., **88**, 175(1975).
29. J.T.B. Ferreira, J.V. Comasseto and A.L. Braga, Synth. Commun., 595(1982) and references therein.
30. J.V. Comasseto, J.T.B. Ferreira, C.A. Brandt and N. Petragnani, J. Chem.

Res. (S), 212(1982), and references therein.
31. J.V. Comasseto, J.T.B. Ferreira and J.A. Fontanillas, J. Organomet. Chem., **277**, 261(1984).
32. J.V. Comasseto, E.S. Lang, J.T.B. Ferreira, F. Simonelli and V.R. Correa, J. Organomet. Chem., **334**, 329(1967).
33. E.S. Lang and J.V. Comasseto, Synth. Commun., **18**, 301(1988).
34. N. Petragnani, Tetrahedron, **11**, 15(1960).
35. R.A. Zingaro, N. Petragnani and J.V. Comasseto, Organometallic Synthesis, vol.3, R.B. King and J.J. Eisch (Ed.), Elsevier, 1986.
36. J. Bergmon, Tetrahedron, **28**, 3323(1972).
37. W.H.H. Günther, J. Nepywoda and J.Y.C. Chu, J. Organomet. Chem., **74**, 79(1974).
38. M.M. Campos and N. Petragnani, Tetrahedron, **18**, 527(1962).
39. S. Uemura, H. Miyoshi and M. Okano, Chem. Lett., 1357(1979).
40. M.M. Campos and N. Petragnani, Tetrahedron, **18**, 521(1962).
41. L. Engaman, J. Amer. Chem. Soc., **106**, 3977(1984).
42. J.E. Bäckvall, J. Bergman and L. Engman, J. Org. Chem., **48**, 3918(1983).
43. L. Engman, Organometallics, **5**, 427(1986).
44. N. Petragnani, L. Torres, K.J. Wynne, J. Organomet.Chem., **92**, 185(1975).
45. For recent examples see: a) L. Engman and A. Hallberg, J. Org. Chem., **54**, 2964(1989); b) K. Giselbrecht, B. Bildstein and F. Sladky, Chem. Ber., **122**, 1255(1989).
46. M.J. Dabdoub and J.V. Comasseto, unpublished results.
47. a) T. Fukumoto, T. Matsuki, N.X. Hu, Y. Aso, T. Otsubo and F. Ogura, Chem. Lett.; 2269(1990). b) For a review see: N.X. Hu, Y. Aso, T. Otsubo and F. Ogura, Phosphorus and Sulfur, 38, 177(1988).
48. N. Petragnani and G. Vicentini, Univ. São Paulo, Faculdade de Filosofia Ciências e Letras. Boletim nº 249 - Química nº 5, 75 (1959).
49. M. M. Campos, N. Petragnani and C. Thomé, Tetrahedron Lett., 5(1960).
50. S.V. Ley, C.A. Meerholz, D.H.R. Barton, Tetrahedron, Suppl. **9**, 37, 213(1981).
51. S.M. Barros, M.J. Dabdoub and J.V. Comasseto, Organometallics, 8, 1661(1989).
52. a) K. Ohe, H. Takahashi, S. Uemura and N. Sugita, J. Org. Chem., **52**, 4859(1987). b) K. Ohe, S. Uemura, N. Sugita, H. Masuda and T. Taga, J. Org. Chem., **54**, 4169(1989).
53. K. Ohe, H. Takahashi, S. Uemura and S. Sugita, Nippon Kagaku Kaishi, 1469(1987).
54. K. Ohe, H. Takahashi, S. Uemura and N. Sugita, J. Organomet. Chem., 326, 35(1987).
55. B.A. Trofimov, N.K. Gusarova, A.A. Tatarinova, V.A. Potapov, L.M. Sinegovskaya, S.V. Amosova and M.G. Voronkov, Tetrahedron, **44**, 6739(1988) and references therein.
56. E.A. Meyers, R.A. Zingaro, M.J. Dabdoub, V.B. Dabdoub, J.V. Comasseto and N. Petragnani, Acta Cryst., **C44**, 1805 (1988).
57. M.J. Dabdoub, J.V. Comasseto and A.L. Braga, Synth.Commun., **18**, 1979(1988).
58. J.V. Comasseto, H.A. Stefani, A. Chieffi and J.Z. Schpector, Or-

ganometallics, **10**, 845(1991).
59. J.Z. Schpector, E.E. Castellano, G. Oliva, J.V. Comasseto and H.A. Stefani, Acta Cryst. **C47**, 000(1991).
60. G. Cardillo and M. Orena, Tetrahedron, **46**, 3321(1990).
61. M.M. Campos and N. Petragnani, Tetrahedron Lett., 11(1959).
62. J.V. Comasseto and N. Petragnani, Synth. Commun., **13**, 889(1983).
63. J.V. Comasseto, H.M.C. Ferraz, N. Petragnani and C.A. Brandt, Tetrahedron Lett., **28**, 5611(1987).
64. J. Bergman and L. Engman, J. Amer. Chem. Soc., **103**, 5196(1981).
65. L. Engman, Organometallics, **8**, 1997(1989).
66. N.X. Hu, Y. Aso, T. Otsubo and F, Ogura, J. Org. Chem., **54**, 4391(1989).
67. N.X. Hu, Y. Aso, T. Otsubo and F. Ogura, J. Org. Chem., **54**, 4398(1989).
68. J.V. Comasseto and coworkers, unpublished results.
69. J.V. Comasseto and M. Grazzini, unpublished results.
70. J.V. Comasseto, H.M.C. Ferraz, C.A. Brandt and K.K. Gaeta, Tetrahedron Lett., **30**, 1209(1989).
71. N. Petragnani, Tetrahedron, **12**, 219(1961).
72. I.D. Sadekov, A.A. Maksimenko and B.B. Rivkin, J. Org. Chem. USSR (Engl.Transl), **14**, 810(1978).
73. L. Engman, Organometallics, **5**, 427(1986).
74. H.A. Stefani, J.V. Comasseto and N. Petragnani, Synth. Commun., **17**, 443(1987).
75. H.A. Stefani, A. Chieffi and J.V. Comasseto, Organometallics, **10**, 1178(1991).
76. a) S. Uemura, K. Ohe and S.I. Fukuzawa, Tetrahedron Lett., **26**, 895(1985). b) S. Uemura and K. Ohe, J. Chem. Soc. Chem. Commun., 1037(1985).
77. a) S. Uemura, S. Fukuzawa and A. Toshimitsu, Tetrahedron Lett., **23**, 1177(1982). b) S. Uemura, S. Fukuzawa and A. Toshimitsu, J. Organomet. Chem., **250**, 203(1983).
78. F. Ogura, Chem. Lett., 447(1981).
79. S. Uemura, S. Fukuzawa and K. Ohe, Tetrahedron Lett., **26**, 921(1985).
80. D.L.J. Clive, G.J. Chittattu, U. Farina, W.A. Kiel, S.M. Menchen, C.G. Russell, A. Singh, C.K. Wong and N.J. Curtis, J. Amer. Chem. Soc., **102**, 4438(1980).
81. V. Franzen and C. Mertz, Liebigs Ann. Chem., **643**, 24(1961).
82. D. Hellwinkel and G. Fahrbach, Chem. Ber., **101**, 574(1968).
83. D. Seebach and A.K. Beck, Chem. Ber., **108**, 314(1975).
84. J. Bergman and L. Engman, J. Organomet. Chem., **199**, 377(1980).
85. J. Bergman and L. Engman, J. Amer. Chem. Soc., **103**, 2715(1981).
86. T. Kauffmann and H. Ahlers, Chem. Ber., **116**, 1001(1983).
87. T. Hiiro, N. Kambe, A. Ogawa, N. Miyoshi, S. Murai and N. Sonoda, Angew. Chem. Int. Ed. Engl., **26**, 1187(1987).
88. T. Hiiro, T. Mogami, N. Kambe, S.I. Fujiwara and N. Sonoda, Synth. Commun., **20**, 703(1990).
89. S.M. Barros, J.V. Comasseto and J.N. Berriel, Tetrahedron Lett., **30**, 7353(1989).
90. T. Hiiro, Y. Morita, T. Inohue, N. Kambe, A. Ogawa, I. Ryu and N. Sonoda, J. Amer. Chem. Soc., **112**, 455(1990).

91. C.A. Brandt , J.V. Comasseto, W. Nakamura and N. Petragnani, J. Chem. Res.(S), 156(1983).

92. T. Hiiro, Y. Atarashi, N. Kambe, S. Fujiwara, A. Ogawa, I. Ryn and N. Sonoda, Organometallics, **9**, 1356(1990).

93. J.V. Comasseto and J.N. Berriel, Synth. Commun., **20**, 1681(1990).

94. G. Vicentini, Chem. Ber., **91**, 801(1956).

95. S. Uemura and S. Fukuzawa, Chem. Lett., 943(1980).

96. K. Chikamatsu, T. Otsuko, F. Ogura and H. Yamaguchi, Chem. Lett., 1081(1982).

97. H.K. Spencer, M.V. Lekshmikantan and M.P. Cava, J. Amer. Chem. Soc., **99**, 1470 (1977).

98. K. Spencer, M.P. Cava, J. Org. Chem., **42**, 2937(1977).

99. S. Uemura, S.J. Fukuzawa, M. Wakasugi, M. Okano, J. Organomet. Chem., **214**, 319(1981).

100. M.J. Dabdoub, J.V. Comasseto, S.M. Barros and F. Moussa, Synth.. Commun., **20**, 2181(1990).