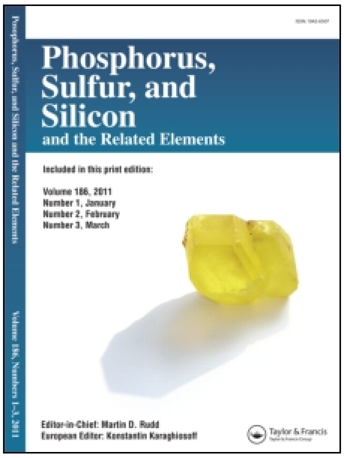

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TELLURIUM IN ORGANIC SYNTHESIS

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An overview of tellurium reagents in organic synthesis is presented.

Keywords: tellurium reagents

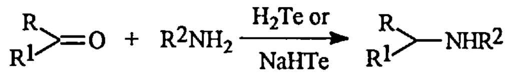
INTRODUCTION

Over a quarter of century ago, Tellurium was considered almost as an exotic element and treated with certain diffidence. But then the explosive development of Selenium chemistry called attention to the potentiality of Tellurium analogues. A relevant increasing number of transformations based on Tellurium species are currently known. Herein is an overview of their most important applications in Organic Synthesis[1].

REDUCTION

Many organic substrates can be reduced by tellurium reagents. The most useful ones are: H_2Te, NaHTe, Na_2Te, PhTeH and PhTeNa[2]. They offer some advantages over the conventionals such as milder reaction conditions, high regioselectivity, in situ preparation, sometimes in catalytic conditions, and the recovery of tellurium in elemental form or as Ph_2Te_2.

Aldehydes and ketones can be reduced to the corresponding alcohols by in situ generated H_2Te, PhTeH and Ti (III) species, this latter from the $Bu_2Te/TiCl_4$ system[3]. Selective reduction of C=C bond of α,β-unsaturated carbonyl compounds is achieved by treatment with H_2Te, PhTeH and NaHTe. Imines and enamines are reduced to the corresponding amines. An interesting and useful application is the one-step reductive alkylation of amines with carbonyl compounds[4] (Equation 1).



(1)

Oxiranes undergo deoxigenation to alkenes by either $(EtO)_2P(O)TeNa(Li)$[5] or NaHTe[6] in a stereoselective manner or by a two-step methodology, respectively (Scheme 1). α,β-Epoxyketones are easily reduced to the corresponding β-hydroxy ketones by NaHTe[7].

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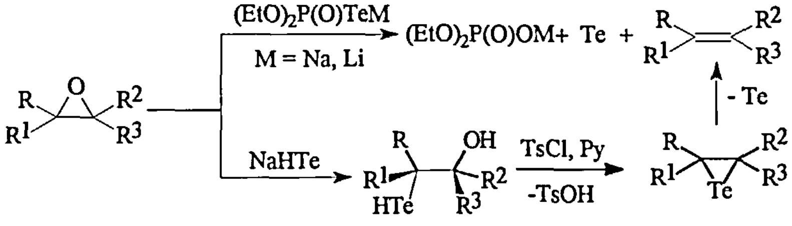
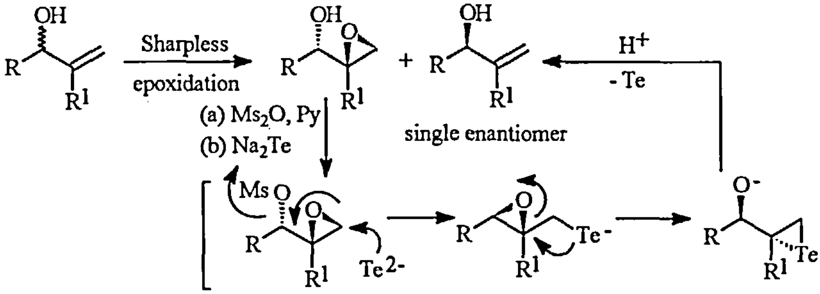


SCHEME 1

Epoxides bearing leaving groups in suitable position are converted to allylic alcohols via an intermediate epitelluride. This methodology, combined with Sharpless kinetic resolution, provides a useful procedure for an enantioconvergent deracemization of secondary allylic alcohols[8] (Scheme 2).



SCHEME 2

Debromination of vicinal dibromides to alkenes can be achieved by Ar_2Te, Ar_2Te_2, NaHTe, Na_2Te, $(EtO)_2P(O)TeNa$, 2-ThTeNa and $(Ph_3Sn)_2Te$ in typical *anti*-E_2 elimination[9]. The advantages over the conventional methods are mild experimental conditions, high yields, lack of side reactions and inertness of many funcional groups toward the tellurium reagents.

FORMATION OF ANIONIC SPECIES AND REACTION WITH ELECTROPHILES

Nucleophilic attack of Na_2Te at the halogen on α-halo esters or nitriles generates the corresponding carbanions which react with aldehydes giving α,β-unsaturated compounds according to a Reformatsky-type reaction[10]. Bu_2Te promotes in situ·generation of $Ph_3P{=}CH_2$ from the parent phosphonium iodide for further Wittig methylenation reactions[11].

DEPROTECTION OF ORGANIC FUNCTIONALITIES

Anionic tellurium reagents are also useful for the regeneration of protected functional groups, as proceeding under mild conditions in non-hydrolytic medium. For instance, carboxylic acids protected as alkyl or benzyl esters[12] can be regenerated by NaHTe, Na_2Te and Na_2Te_2, and amines protected as trichloro-*t*-butyl carbamates can be regenerated by 2-ThTeNa[13].

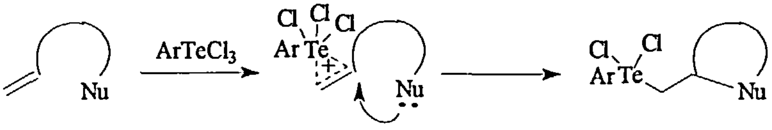
OXIDATION

An_2TeO is an easily prepared, stable crystalline compound which was successfully employes as a mild and selective oxidizing reagent, with the advantage of possible regeneration after the oxidative process.

ArTeO)$_2$O have recently been introduced as oxidizing reagents[14] and are similar to the former oxidant. An important transformation is the oxidation of thio and seleno carbonyl compounds to the oxo-analogs.

TELLURO CYCLOFUNCTIONALIZATION

The addition of $ArTeCl_3$ to olefins bearing a carboxy or a hydroxy group at suitable position followed by intramolecular trapping of the so-formed telluronium intermediate furnishes dichloro telluro lactones[15] and cyclic ethers[16], respectively (Scheme 3). Other useful reagents for these cyclizations are: $PhTeOSO_2C_6H_4NO_2$-4 for the lactonizations and etherifications, and ArTe(O)OAc, TeO_2/AcOH/LiCl and TeO_2/HCl/MeOH for the etherifications.



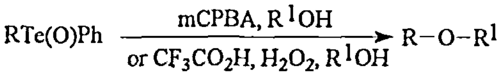
SCHEME 3

CONVERSION OF ORGANOTELLURIUM COMPOUNDS INTO TELLURIUM FREE ORGANIC COMPOUNDS

$ArTeCl_3$ and Ar_2TeCl_2, bearing a *para*-electron-donating group on the aromatic ring, undergo Te/I exchange in the presence of fluoride anions through an electrophilic mechanism[17]. Similar reaction has been perfomed on vinylic tellurium trichlorides with I_2 or NBS.

The *ipso*-substitution (or α-elimination) in tellurium(IV) halides, i.e. selective transfer of a halogen from tellurium to the carbon moiety[18] can be performed by oxidative, photolytic and pyrolytic procedures depending on the tellurium substrates.

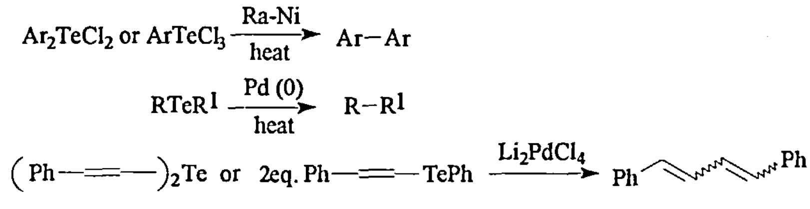
Treatment of telluroxides with excess mCPBA or CF_3CO_3H in alcohols leads to detelluration and formation of alkyl ethers (Scheme 4). Alkyl phenyl tellurones, obtained by oxidation of the telluroxides with $NaIO_4$, give similar results under same conditions[19].



$$RTe(O)Ph \xrightarrow[\text{or } CF_3CO_2H,\ H_2O_2,\ R^1OH]{\text{mCPBA, } R^1OH} R-O-R^1$$

SCHEME 4

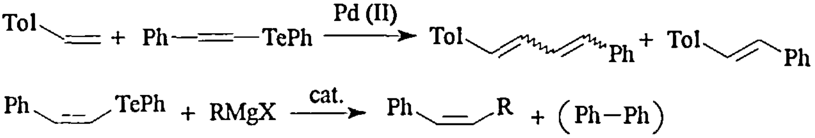
The detellurative coupling reaction on organotellurium compounds can be performed with Ra-Ni[20], Pd (0)[21] or Li_2PdCl_4[22] (Scheme 5).



SCHEME 5

Alkenes bearing electron-withdrawing groups undergo arylation or vinylation by treatment with Ar_2TeCl_2, $ArTeCl_3$, Ar_2Te or vinyl tellurides[23] in the presence of $PdCl_2$ or $Pd(OAc)_2$ (Scheme 6). These cross-coupling reactions can be carried out with catalytic amounts of Pd

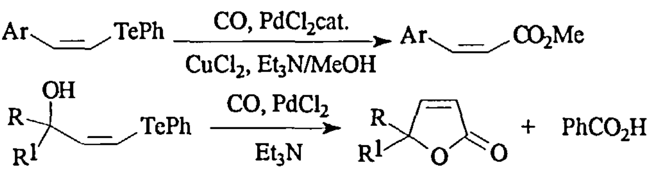
(II) salts in the presence of a suitable oxidant such as *t*-BuOOH, $CuCl_2$ or AgOAc. Under Ni (II) or Co (II) phosphine complex catalysis, some organo tellurides react with Grignard reagents leading to either cross-coupled and homo-coupled products[24] (Scheme 6).



cat. = $NiCl_2(PPh_3)_2$, $CoCl_2(PPH_3)_2$, $NiCl_2.Ph_3(CH_2)_3PPh_3$

SCHEME 6

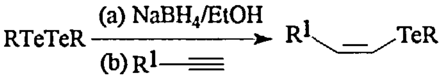
Pd (II) also promotes detellurative carbonylations[25] of alkyl, vinyl, alkynyl and phenyl tellurides with $CO/MeOH/Et_3N$ giving methyl carboxylates. While performed in the presence of $CuCl_2$ as oxidant, only catalytical amount of Pd (II) is needed. The same methodology is also suitable to prepare substituted butenolides starting from hydroxy vinyl tellurides (Scheme 7).



SCHEME 7

VINYLIC TELLURIDES

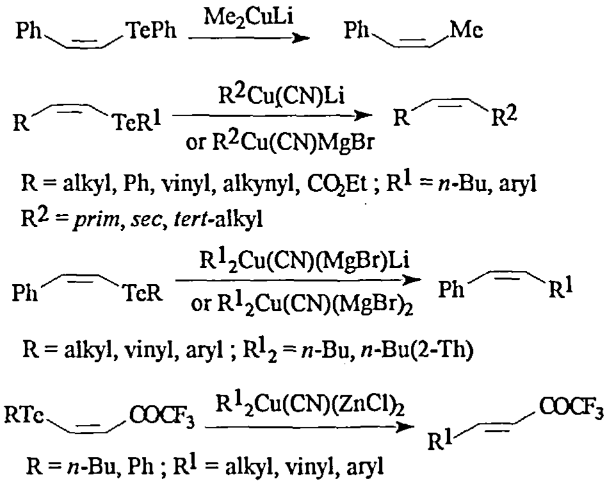
Vinylic tellurides are important compounds due to their peculiar behavior as synthons and intermediates. The general preparative procedure is addition of organyl tellurolates, obtained by reduction of the corresponding ditellurides with sodium borohydride, to acetylenes[26] This addition is highly stereoselective, occurring exclusively in an *anti* mode giving the *Z* adducts (Scheme 8), in sharp contrast to the well known hydrostannylation, hydrozirconation and hydroalumination of acetylenes, which in turn are characterized by *syn* addition modes leading to *E* adducts.



R^1 = alkyl, aryl, CO_2Et, vinyl, alkynyl

SCHEME 8

Detellurative cross-coupling reaction of vinylic tellurides with retention of the double bond geometry (Scheme 9), has been performed by reaction with several lithium and/or magnesium, higher and lower order cuprates[27]. Exceptionally, zinc cyanocuprates[27d] promote similar reaction with complete inversion of the double bond geometry in the coupled products (Scheme 9).



R = alkyl, Ph, vinyl, alkynyl, CO_2Et ; R^1 = *n*-Bu, aryl
R^2 = *prim*, *sec*, *tert*-alkyl

R = alkyl, vinyl, aryl ; R^1_2 = *n*-Bu, *n*-Bu(2-Th)

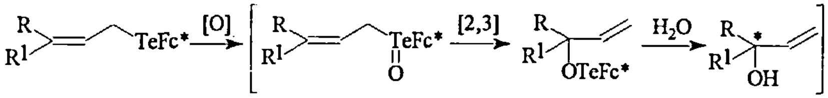
R = *n*-Bu, Ph ; R^1 = alkyl, vinyl, aryl

SCHEME 9

OLEFIN SYNTHESIS

Although not so well known as the familiar *syn*-selenoxide elimination, the corresponding telluroxide elimination[28] has recently gained more attention among the olefin synthesis methodologies. This elimination, which is preferential towards the less substituted carbon, can occur either at room temperature or upon heating over 200°C depending on the starting telluroxide.

Allylic telluroxides undergo [2,3]-sigmatropic rearrangements[29] furnishing allylic alcohols after hydrolysis. The same sequence when performed on chiral allylic ferrocenyl tellurides leads to chiral allylic alcohols via chirality transfer (Scheme 10).



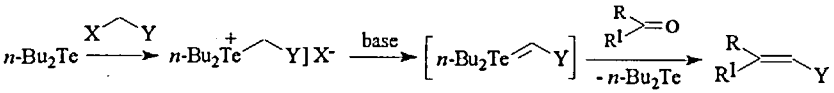
[O] = t-BuOOH, $NaIO_4$, H_2O_2, O_2 ; Fc* = ferrocenyl

ee = 14-22%

SCHEME 10

Treatment of telluronium salts bearing electron-withdrawing groups with bases furnishes telluronium ylides, which can undergo Wittig-type olefination reactions with a variety of carbonyl compounds[30] (Scheme 11).

Stabilized telluronium ylides

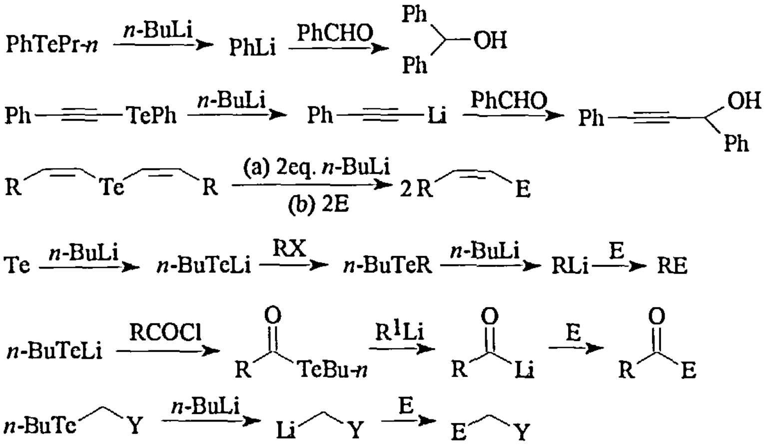


X = Cl, Br ; Y = CO_2Et, COPh, CN, CONHBu-i, Ph ; base = t-BuOK, NaH/HMPA

SCHEME 11

TRANSMETALATION REACTION

By treating diorganyl tellurides with alkyllithiums, a Te/Li exchange reaction takes place generating the most stable organolithium derivative[31]. This transmetalation is very useful for the preparation of lithium reagents which cannot be achieved by conventional methods such as allyl, benzyl, propargyl, acyl, aroyl and heteroatom substituted methyllithiums. The Te/Li exchange in vinylic tellurides occurs with retention of the original *Z* geometry of the C=C bond furnishing therefore a useful methodology for the preparation of *Z*-vinyllithiums. The resulting new organolithiums can be trapped with a large variety of different electrophiles, such as aldehydes, ketones, CO_2, acid chloride, halide and silyl chloride, as shown in the following representative examples (Scheme 12).

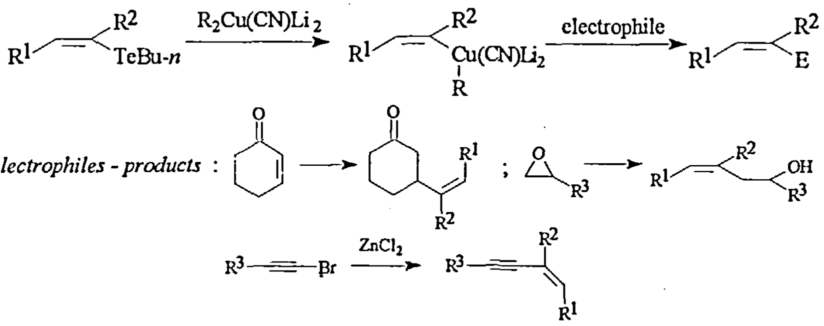


Y = $PhCH_2O$, $MeO(CH_2)_2O$, Me_2N, Me_3Si, BuTe, PhSe, Bu_3Sn

SCHEME 12

Transmetalations with Na, K, Mg and Ca have been performed on alkyl, alkenyl, aryl, allyl and benzyl tellurides[32], while Te/Zn exchange reaction[33] followed by coupling with aryl iodide was achieved under palladium catalysis.

The most promising synthetic application of Z-vinylic tellurides is their transmetalation with higher order cyanocuprates. The counter-ion in the cuprate plays an important role in this reaction. Instead of detelluratirve cross-coupling reaction observed with lithium-magnesium and di-magnesium derivatives, the dilithium cyanocuprate promotes Te/Cu exchange giving higher order vinylic cyanocuprates with retention of the original double bond geometry. The resulting Z-vinylic cuprates readily perform conjugate addition[34] to α,β-unsaturated ketones, epoxide opening and coupling reaction with bromo alkynes in the presence of $ZnCl_2$ (Scheme 13).

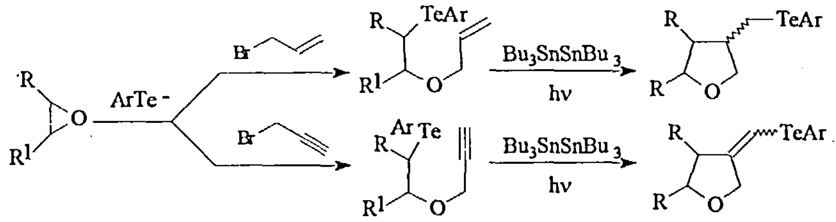


SCHEME 13

There are also some special higher order cyanocuprates such as dimethyl, (2-thienyl,butyl) and (imidazoyl,butyl) dilithium cyanocuprates which carries the so-called "dummy ligands" that are non-transferable from the cuprate, therefore avoiding formation of undesired addition by-products.

FREE RADICAL CHEMISTRY

By treatment with Li_2Te, allylic halides are converted into 1,5-dienes[35] by coupling reaction of the corresponding allylic radicals. Upon irradiation of a mixture containing the acetyl derivative of N-hydroxy-2-thiopyridone, alkyl anisyl telluride and and electrophilic olefin, a radical chain mecanism takes place[36], which was used for intramolecular radical cyclizations to six-membered rings and also in tellurium mediated addition of carbohydrates to olefins. Recently telluro methyl and telluro methylene substituted tetrahydrofurans were obtained from epoxides by the combination of tellurolate promoted epoxide opening and radical cyclizations[37] (Scheme 14).



SCHEME 14

Acknowledgments

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