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A general method of synthesis of functionalized *Z*-vinylic tellurides starting from β-dicarbonyl compounds

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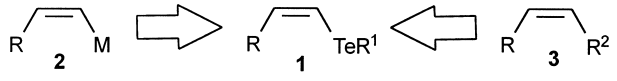
Abstract—*Z*-Vinylic tellurides are prepared by stereoselective vinylic substitution on *Z*/*E* mixtures of enolphosphates, acetates, tosylates and triflates by organotellurolates. The reaction is sensitive to the nature of the organotellurolate; the aromatic derivatives react slower than the aliphatic ones. The reaction time is not influenced by the nature of the leaving group.

1. Introduction

Tellurium–metal exchange easily transforms vinylic tellurides (**1**) into vinylic species of lithium,[1] sodium,[2] magnesium,[2] calcium,[2] copper[3] and zinc (**2**) with retention of the olefin stereochemistry.[4] Most of these transformations involve *Z*-vinylic tellurides, generated by *anti* hydrotelluration of alkynes. The other methods to generate vinylic organometallics by heteroatom–metal exchange give the *E*-isomers as a consequence of the *syn* nature of hydrometallation of alkynes.[5] Besides the tellurium metal exchange reaction, another useful transformation is the coupling of *Z*-vinylic tellurides with organometallic species giving highly unsaturated systems (**3**) with retention of the *Z* configuration[6] (Scheme 1).

In view of the synthetic potential of vinylic tellurides, the hydrotelluration of alkynes has been widely studied in the last two decades. Since its first report in 1976, this reaction has been performed by reacting alkynes with a mixture of



M = Li,[1] Na,[2] CaI,[2] MgX,[2] $L_2CuCNLi_2$,[3] ZnR,[4a] ZnCl[4b]

R = alkyl, aryl, alkenyl, alkynyl

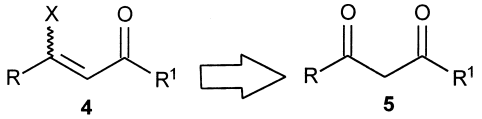
R^2 = alkyl, alkynyl

Scheme 1.

the suitable diorganoditelluride and sodium borohydride in ethanol.[7] Recently we introduced an improvement in this method, substituting the diorganoditelluride by the system *n*-BuTeLi/EtOH to avoid the use of malodorous dialkylditellurides.[8]

These facts transformed the hydrotelluration of alkynes in the method of choice to prepare *Z*-vinylic tellurides. However, in view of the synthetic potential of these organoelemental compounds, it would be interesting to explore other general methods to access them. The vinylic substitution of activated enol derivatives (**4**) by a tellurolate anion could be considered a logical methodology to prepare vinylic tellurides, in view of the easy access to **4** from β-dicarbonyl compounds (**5**), as well as due to the stereospecificity of the vinylic substitution (Scheme 2).[9]

However, the number of works dealing with vinylic substitution involving tellurium nucleophiles is small. To our knowledge, the first mention to a vinylic substitution by a tellurolate anion was made by our laboratory in 1986.[10] In this work we showed that organotellurolate anions generated by reduction of the corresponding diorganoditelluride (**6**) with lithium aluminum hydride react with *E*-β-bromostyrene (**7**) to give the corresponding *E*-1-organotelanyl-2-phenyl ethene (**8**).[10] Shortly thereafter Uemura



X = Cl, $OC(O)CH_3$, $OS(O)R^2$, $OP(O)(OR^2)_2$

Scheme 2.

Keywords: *Z*-vinylic tellurides; vinylic substitution; tellurium.

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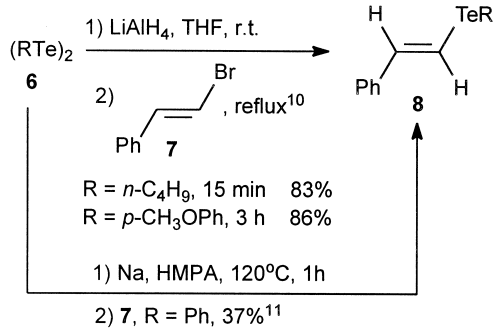
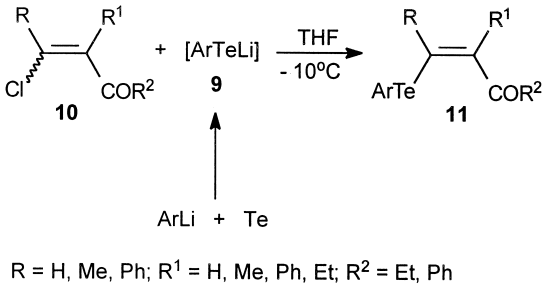


Scheme 3.

reported a similar transformation using Na/HMPA to reduce the ditelluride to the tellurolate anion.[11] The results shown in Scheme 3 indicate that the alkyltellurolate reacts faster than the aromatic ones.

The first extensive study on the vinylic substitution by organotellurolates (**9**) on activated vinylic halides (**10**) leading to functionalized vinylic tellurides (**11**), was reported by Minkin et al. in 1997.[12] The metal organotellurolates (**9**)



Scheme 4.

were generated by reacting aryllithiums with elemental tellurium (Scheme 4).

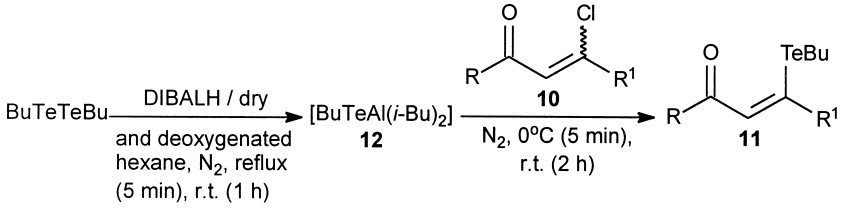
This study showed that only the *Z* isomer was formed, even starting from a mixture of *Z* and *E* vinylic halides (**10**). This result was surprising, since the vinylic substitution reaction usually occurs with retention of the double bond geometry.[9]

Similar findings were obtained in our laboratory using [BuTeAl(*i*-Bu)$_2$] (**12**) as the nucleophile (Scheme 5).[13]

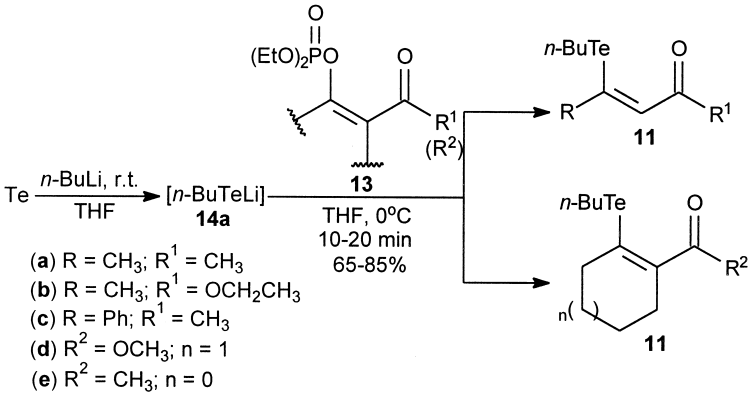
The results described earlier showed that the vinylic substitution is a potentially very useful reaction to prepare functionalized *Z*-vinylic tellurides. In view of this fact we decided to explore the substitution reaction using enol derivatives of β-dicarbonyl compounds (**4**), which are easily prepared under very mild basic conditions.

2. Results and discussion

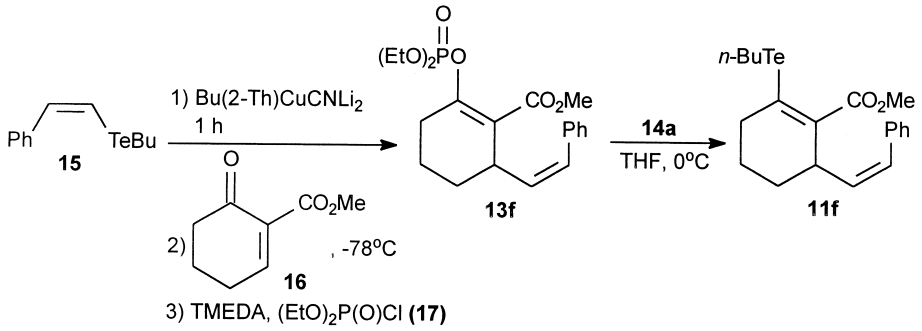
In the present work we initiated[14] the study with activated enolphosphates (**13**) which were prepared by described methods.[15] The reaction consisted in the in situ formation of the lithium *n*-butyltellurolate (**14a**) by reaction of *n*-BuLi with elemental tellurium in THF at room temperature. To the resulting clear yellow solution was added the enolphosphate (**13**) at 0°C. The reaction is very fast and the functionalized vinylic tellurides (**11**) were obtained in good yields after purification by silica gel chromatography (Scheme 6). It is worthy of note that the lithium *n*-butyltellurolate is prepared from commercial *n*-butyllithium and elemental tellurium, avoiding the use of malodorous and commercially unavailable tellurium reagents. All compounds were obtained as yellow oils. The spectroscopic analysis (^{1}H, ^{13}C NMR and GC–MS) of all compounds showed that only one isomer of the telluride was formed.



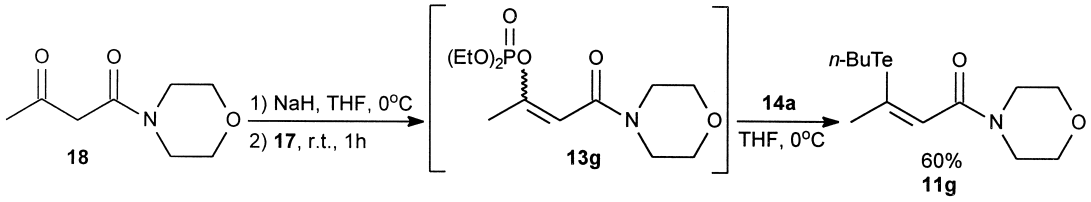
Scheme 5.



Scheme 6.



Scheme 7.



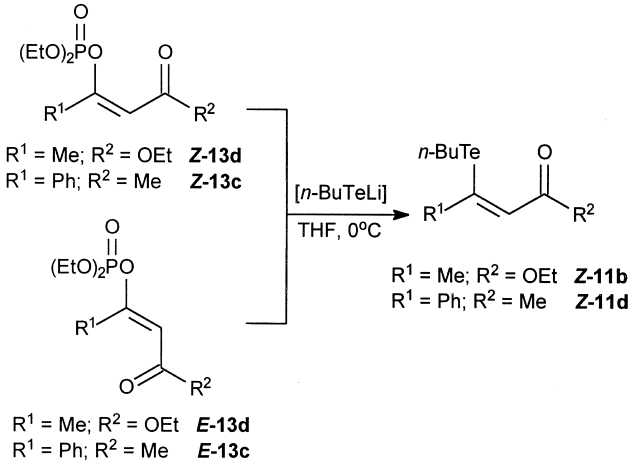
Scheme 8.

NOEDS experiments for compounds **11a–c** showed that the stereochemistry of the resulting tellurides was *Z* as will be discussed later.

In one case the enolphosphate (**13f**) was prepared by reaction of methyl-6-oxo-1-cyclohexene-1-carboxylate (**16**) with dilithium (2-thienyl)-[(*Z*)-2-phenylethene]cyanocuprate, prepared by transmetallation of 1-butyltelanyl-2-phenyl ethene (**15**) with dilithium *n*-butyl-(2-thienyl)-cyanocuprate,[3f] followed by capture of the resulting enolate with diethylphosphorochloridrate (**17**) (Scheme 7).[16]

Reaction of the isolated **13f** with **14a** gave the highly functionalized vinylic telluride **11f**.

An interesting variation of the above methodology consisted in the in situ generation of the enolphosphate **13g**, followed by the transfer via canula of the preformed **14a** to the solution of the enolphosphate **13g** (Scheme 8).



Scheme 9.

The overall yield of this one pot procedure was similar to the one of the two steps sequence involving the isolation and purification of the enolphosphates **13**. The product **11g** was obtained as a pale yellow crystalline solid and its structure was determined by X-ray analysis.

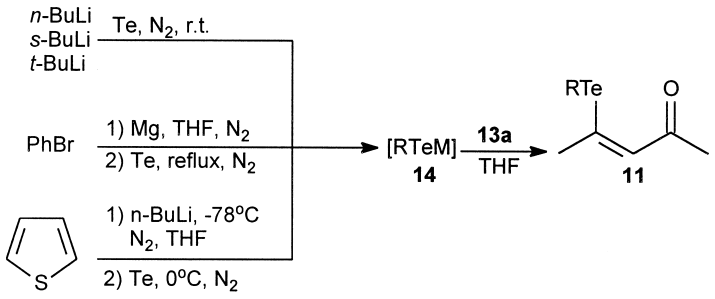
In order to confirm the stereoselectivity of the reaction, the *Z* and *E* diastereomers of the enolphosphates **13c**,**d** were separated by chromatography in silica gel and both isomers were separately reacted with *n*-BuTeLi. The same products *Z*-**11b** and *Z*-**11c** were obtained in both cases (Scheme 9).

In this way, it was confirmed that the reaction is highly stereoselective. Starting from pure *E* or *Z* isomers of the enolphosphates **13** or from a *E*/*Z* mixture, only the *Z* vinylic tellurides **11** are obtained.

In view of these encouraging results, we decided to explore the scope of the reaction to determine its generality. Firstly we investigated the influence of the structure of the organotellurolate anion. For this end we chose five different tellurolate anions, *n*-$BuTe^-$ (**14a**), *s*-$BuTe^-$ (**14b**), *t*-$BuTe^-$ (**14c**), $PhTe^-$ (**14d**) and (2-Th)Te^- (**14e**). These organotellurolates were reacted with the same enolphosphate (**13a**) under the reaction conditions indicated in Scheme 10.

Compound **11j** was obtained as a crystalline solid and its structure was determined by X-ray analysis. The remaining tellurides were liquids and their stereochemistry was determined by NOEDS experiments. In all cases the configuration was *Z*. Compounds **11h** and **11i** are unstable in the presence of the air.

The data in Scheme 10 show that the reaction times in the case of phenyl (**14d**) and thienyl (**14e**) tellurolates are longer than the reaction times for the alkyltellurolates (**14a–c**). This observation can be rationalized in terms of a lower electron density on tellurium in **14d** and **14e** due to the



			Yield (%)	Temperature (°C)	Reaction Time (min)
R = *n*-Bu; M = Li	**14a**	**11a**	85	0	10
R = *s*-Bu; M = Li	**14b**	**11h**	70	0	15
R = *t*-Bu; M = Li	**14c**	**11i**	65	0	15
R = Ph; M = MgBr	**14d**	**11j**	60	r.t.	300
R = 2-Th; M = Li	**14e**	**11k**	70	r.t.	300

Scheme 10.

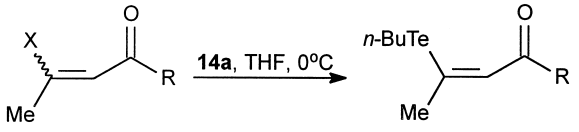
aromatic substitutents. This result is in accordance with that described in Scheme 3. In addition, the data on Scheme 10 show that the reaction is not sensitive to steric factors since the reaction times are similar for the reaction of **14a–c** with **13a**.

In the following we investigated the influence of the leaving group. At the same time we showed that the reaction can be performed with different enolderivatives, and demonstrated the versatility of this method to prepare functionalized *Z*-vinylic tellurides. We chose four representative leaving groups, namely, diethylphosphate (**13**), tosylate (**20**), triflate (**21**) and acetate (**22**), preparing the corresponding derivatives of a β-diketone and a β-ketoester as *E*/*Z* mixtures, which were reacted with **14a** under identical reaction conditions (Scheme 11).

From the above results we can see that the reaction works well with different enol derivatives and no significant difference in reaction times was observed in changing the leaving groups. As in the case with the enolphosphates, starting from mixtures of *E*/*Z* enol derivatives, only the *Z*-vinylic tellurides were obtained.

3. Structure of the resulting vinylic tellurides and mechanistic considerations

As mentioned earlier, the geometry of the liquid vinylic tellurides was determined by NOEDS experiments. As an example, when telluride **11a** was irradiated at the signal attributed to hydrogen H_a (7.2 ppm) the signal at 2.4 ppm attributed to hydrogen H_b, suffered an increment indicating



			Yield (%)	Reaction Time (min)
X = $(EtO)_2P(O)O$; R = Me[14]	**13a**	**11a**	85	10
X = $(EtO)_2P(O)O$; R = OEt[14]	**13b**	**11b**	75	10
X = OTs; R = Me	**20a**	**11a**	75	20
X = OTs; R = OEt	**20b**	**11b**	70	20
X = OTf; R = OEt	**21**	**11b**	80	20
X = OAc; R = Me	**22**	**11a**	80	15

Scheme 11.

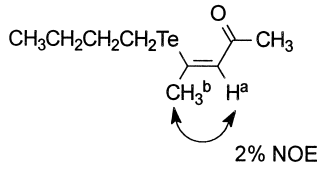


Figure 1. NOEDS experiment for telluride **11a**.

a *cis* relationship between them. The same occurred with the signal at 7.2 ppm when the signal at 2.4 ppm was irradiated (Fig. 1). Similar results were obtained for tellurides **11b** and **11c**.

Two of the obtained vinylic tellurides (**11g** and **11j**) were crystalline solids and were submitted to X-ray analysis. Both compounds presented a *Z* stereochemistry with a strong interaction between the tellurium atom and the carbonyl oxygen indicated by the internuclear distances (2.693 and 2.7346 Å, respectively) which are shorter than the sum of the Van der Waals radii of oxygen and tellurium (3.60 Å)[17] (Fig. 2). Taking the secondary bond into account, the configuration around the Te atom can be described as slightly distorted T-shaped (O···Te–C=168 and 165° for **11g** and **11j**, respectively). These observations corroborate prior reports in this area.[12]

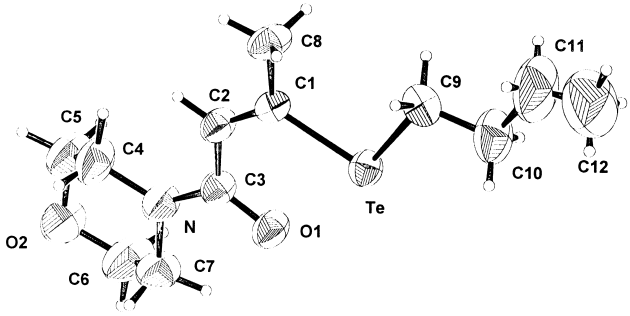


Figure 2. ZORTEP drawing of **11g**. Ellipsoids are shown at the 50% probability scale, except the H-atom that is at an arbitrary scale for a sake of clarity. Only one of the positions for C11 is shown. Selected bond lengths (Å) and angles (deg): Te–C1=2.091 (5), Te–C9=2.153 (6), C1–Te–C9=97.8 (2).

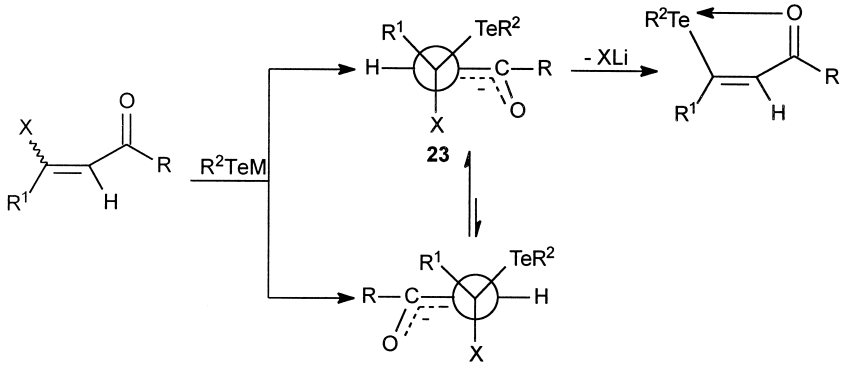
This tellurium–oxygen interaction led Minkin and coworkers to propose an addition–elimination mechanism for the SNv substitution reaction of tellurolate anions on β-chloroenones,[12] in which the rotamer **23** (Scheme 12), responsible for the formation of the *Z*-vinylic telluride, should be favored in the equilibrium, due to a strong Te–O interaction. This fact could explain the high stereoselectivity toward the *Z* isomer, independent of the stereochemistry of the starting vinyl halide. As commented before, we observed the same stereoselectivity for all the leaving groups studied in this work, what seems to support Minkin's mechanistic suggestion.

4. Conclusion

The results reported in this work constitute a general and stereoselective method to prepare functionalized *Z*-vinylic tellurides. The starting materials are easily prepared under mild basic conditions from β-dicarbonyl compounds, and the metal organotellurolates used as nucleophiles are prepared from elemental tellurium and commercially available organometallics, avoiding the use of malodorous tellurium reagents such as dialkylditellurides. These facts make this method attractive to prepare stereodefined vinylic tellurides, compounds of wide synthetic applications for carbon–carbon bond formation.[18]

5. Experimental

^{1}H and ^{13}C NMR spectra were recorded on either a Bruker DPX-300, Bruker DRX-500 or a Bruker AC-200 spectrometers using as internal standard tetramethylsilane and the central peak of $CDCl_3$ (77 ppm), respectively. The ^{125}Te NMR were obtained in a Bruker DRX-500 spectrometer, operating at 157.79 MHz using a 10 mm-BBO probe or a 5 mm-BBI probe without ^{1}H decoupling. The spectral width used was 94.78 kHz with FIDRES 5.78 Hz (0.036 ppm). The chemical shifts reproductibility was ±0.8 ppm keeping the temperature constant (±0.5°C). The functionalized *Z*-vinylic tellurides were dissolved in $CDCl_3$ with a final concentration between 0.1 and 0.5 M. The chemical shifts refer to diphenyl ditelluride $(PhTe)_2$ (δ=420 ppm, 25°C if



X = Cl (**10**), $(EtO)_2P(O)O$ (**13**), *p*-$CH_3PhS(O)_2O$ (**20**), $CF_3S(O)_2O$ (**21**), $CH_3C(O)O$ (**22**)
M = Li, MgBr
R = alkoxy, *N*-alkyl, alkyl; R^1 = methyl, phenyl

Scheme 12.

dimethyl telluride is considered δ=0.0 ppm, 25°C) as external standard. The chemical shifts for the external standard were corrected by 0.237 ppm K^{-1}.[19] Infrared spectra were recorded on a Perkin–Elmer 1600 spectrophotometer. Low resolution mass spectra were obtained on a Finnigan 4021 spectrometer or on a GC–MS-Hewlett Packard 5988-8/5890 spectrometer, both operating at 70 eV. Elemental analysis was performed at the Microanalytical Laboratory of the Chemistry Institute, University of São Paulo. Column chromatography was carried out with Merck silica gel (230–400 mesh). Thin Layer Chromatography (TLC) was performed on silica gel F-254 on aluminum. All solvents used were previously dried and distilled according to the usual methods.[20] THF and diethyl ether were distilled from sodium/benzophenone under N_2, immediately before use. Elemental tellurium (200 mesh) was purchased from Aldrich and dried overnight in an oven at 100°C, CuCN was dried under vacuum in an Abderhalden apparatus over P_2O_5, at 70°C. The following reagents were prepared according to the literature procedures: 1-butyltelanyl-2-phenylethene,[3f] diethylphosphorochloridrate[21] and *N*-phenyl-trifluoromethanesulfonamide.[22] The enolphosphates **13a**–**c**, **e** were prepared according to Ref. 15 as isomeric mixtures (**13a**, *E*/*Z* ratio: 8/1; **13b**, *E*/*Z* ratio: 6/1; **13c**, *E*/*Z* ratio: 15/1 and **13e**, *endo*/*exo* ratio 87/7). Compounds *Z*-**13d**, *Z*-**13c**, *E*-**13d** and *E*-**13c** were obtained as pure isomers by column chromatography separation on silica gel eluting with hexane/ethyl acetate (3/1). A similar procedure[15] was used to prepare enol tosylate **20a** (*E*/*Z* ratio: 6/1) and **20b** (*E*/*Z* ratio: 5/1). Enol triflate **21** was obtained as a single isomer[23] and enol acetate **22** was obtained as a *E*/*Z* mixture in a 1/1 ratio.[24] The remaining chemicals were obtained from commercial sources. All operations were carried out in dried glassware, under an inert atmosphere of dry and deoxygenated N_2. The IUPAC names were obtained using the ACD/Lab web service, version 3.5, at http://www.acdlabs.com/ilab.

5.1. X-Ray crystallography. Collection of the data and structure determination

For all structures data were collected on an Enraf–Nonius CAD4 diffractometer using graphite monochromated Mo K_α radiation (λ=0.71073 Å), room temperature and $\omega/2\theta$ scans. Three standard reflections measured every 30 min showed, in all cases only random deviations. Lp correction and semiempirical absorption corrections derived from ψ-scans were applied. The structures were solved using direct methods and refined by full-matrix least-squares based on F^2. Hydrogen atoms were located on stereochemical grounds and refined using a riding model with U(H)=1.5U_{eq}(C) for methyl and 1.2U_{eq}(C) for other groups. For data collection and cell refinement the CAD-4 Software was used;[25] data reduction was performed using MolEN.[26] Program used to solve the structures SHELXS86[27] and SHELXL97[28] to refine them. The molecular graphics program ZORTEP[29] was used. Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC 174910 (**11j**) and CCDC 174911 (**11g**).

5.2. General procedure for the substitution reactions between activated enols and lithium *n*-butyltellurolates

To a suspension of elemental tellurium (0.38 g, 3 mmol) in THF (4 mL) under nitrogen at 0°C was slowly added *n*-butyllithium (from a 1.4 M solution in hexane, 2.1 mL, 3 mmol). A clear yellow solution was formed. Then the appropriate (**13**, **20**, **21** or **22**) enol was added (2 mmol) and the mixture was stirred at 0°C monitoring by TLC, until the consumption of the enol (for reaction times and yields Schemes 6, 7, 10 and 11). The reaction mixture was diluted with ethyl acetate (50 mL) and washed with brine (3×50 mL). The organic phase was dried with magnesium sulfate and the solvents were evaporated. The residue was purified by silica gel column chromatography eluting with hexane/ethyl acetate (9/1).

5.2.1. (*Z*)-4-(*n*-Butyltelanyl)-3-penten-2-one (11a). ^{1}H NMR ($CDCl_3$, 500 MHz) δ (ppm) 7.19 (quart., *J*=0.9 Hz, 1H); 2.59 (t, *J*=7.4 Hz, 2H); 2.44 (d, *J*=0.9 Hz, 3H); 2.17 (s, 3H); 1.72 (quint., *J*=7.4 Hz, 2H); 1.42 (sext., *J*=7.4 Hz, 2H); 0.93 (t, *J*=7.4 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm): 196.3; 152.6; 129.0; 33.2; 29.8; 27.3; 25.3; 13.5; 6.1; ^{125}Te NMR ($CDCl_3$, 157.79 MHz) δ (ppm) 651; LR-MS *m*/*z* (rel. int.): 268 (13)(M^+); 213 (100); 171 (5); 128 (5); 83 (31); IR (neat) ν (cm^{-1}) 2957; 2925; 1647; 1527; 1199; Anal. calcd for $C_9H_{16}OTe$: C, 40.36; H, 6.02; Found: C, 40.89; H, 6.03.

5.2.2. Ethyl (*Z*)-3-(*n*-butyltelanyl)-2-butenoate (11b). See Ref. 14.

5.2.3. (*Z*)-4-(*n*-Butyltelanyl)-4-phenyl-3-buten-2-one (11c). ^{1}H NMR ($CDCl_3$, 500 MHz) δ (ppm) 8.01–7.99 (m, 2H); 7.96 (quart., *J*=1.2 Hz, 1H); 7.53–7.44 (m, 3H); 2.65 (t, *J*=7.7 Hz, 2H); 2.60 (d, *J*=1.2 Hz, 3H); 1.76 (quint., *J*=7.7 Hz, 2H); 1.45 (sext., *J*=7.7 Hz, 2H); 0.95 (t, *J*=7.7 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ (ppm) 188.6; 157.0; 138.3; 132.2; 128.6; 127.9; 125.2; 33.0; 28.0; 25.4; 13.5; 6.9; LR-MS *m*/*z* (rel. int.) 275 (100); 145 (20); 105 (70); 77 (85); IR (neat) ν (cm^{-1}) 3058; 2957; 2923; 1614; 1575; 1518; 1238; 1059; 774; 699; Anal. calcd for $C_{14}H_{18}OTe$: C, 50.97; H, 5.50; Found: C, 50.69; H, 5.39.

5.2.4. Methyl-2-(*n*-butyltellanyl)-1-cyclohexen-1-carboxylate (11d). ^{1}H ($CDCl_3$, 500 MHz) δ (ppm) 3.76 (s, 3H); 2.57–2.54 (m, 4H); 2.39–2.38 (m, 2H); 1.74–1.68 (m, 6H); 1.42 (sext., *J*=7.4 Hz, 2H); 0.93 (t, *J*=7.4 Hz, 3H); ^{13}C ($CDCl_3$, 125 MHz) δ (ppm) 169.3; 140.8; 127.4; 51.8; 34.6; 33.2; 27.8; 25.4; 24.0; 21.9; 13.5; 6.3; ^{125}Te NMR ($CDCl_3$, 157.79 MHz) δ (ppm) 578; LR-MS *m*/*z* (rel. int.) 214 (27); 141 (100); 89 (2); IR (neat) ν (cm^{-1}) 2930; 2858; 1678; 1566; 1435; 1279; 1253; 1058; Anal. calcd for $C_{12}H_{20}O_2Te$: C, 44.50; H, 6.22; Found: C, 45.00; H, 6.11.

5.2.5. 1-[2-*n*-Butyltelanyl]-cyclopentenyl]-1-etanone (11e). ^{1}H ($CDCl_3$, 500 MHz) δ (ppm) 2.81–2.77 (m, 2H); 2.74–2.70 (m, 2H); 2.58 (t, *J*=7.6 Hz, 2H); 2.15–2.09 (m, 2H); 1.74 (quint., *J*=7.6 Hz, 2H); 1.40 (sext., *J*=7.6 Hz, 2H); 0.94 (t, *J*=7.6 Hz, 3H); ^{13}C ($CDCl_3$, 125 MHz) δ (ppm) 195.9; 146.7; 141.1; 39.9; 33.9; 33.7; 28.4; 25.3; 25.0; 13.5; 5.9; LR-MS *m*/*z* (rel. int.): 296 (13)(M^+); 239 (100);

95 (8); 67 (32); IR (neat) ν (cm^{-1}) 2955; 2926; 1635; 1522; 1361; 1267; Anal. calcd for $C_{11}H_{18}OTe$: C, 44.96; H, 6.17; Found: C, 45.14; H, 6.13.

5.2.6. Methyl-6-[(*Z*)-2-phenylethenyl]2-(*n*-butyltelanyl)-1-cyclohexen-1-carboxylate (11f). ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.38–7.23 (m, 5H); 6.39 (d, J=11.4 Hz, 1H); 5.60 (dd, J=11.4, 10.8 Hz, 1H); 4.02–3.99 (m, 1H); 3.49 (s, 3H); 2.78–2.71 (m, 1H); 2.58–2.50 (m, 3H); 1.86–1.84 (m, 3H); 1.72–1.63 (m, 3H); 1.41 (sext., J=7.2 Hz, 2H); 0.96 (t, J=7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 169.5; 141.9; 138.1; 135.4; 130.2; 128.7; 128.5; 128.3; 126.7; 51.7; 35.8; 34.9; 33.4; 29.2; 25.6; 20.9; 13.7; 6.7; ^{125}Te NMR ($CDCl_3$, 157.79 MHz) δ (ppm) 587; LR-MS m/z (rel. int.) 324 (28); 267 (100); 137 (16); 105 (35); 77 (35); IR (neat) ν (cm^{-1}) 3007; 2953; 2930; 2870; 1715; 1678; 1435; 1273; 1255; 702; Anal. calcd for $C_{20}H_{26}O_2Te$: C, 56.39; H, 6.15; Found: C, 56.74; H, 6.50.

The same general procedure described above was followed to prepare compounds **11h** and **11i**, substituting *n*-butyllithium for *s*-butyllithium and *t*-butyllithium, respectively.

5.2.7. (*Z*)-4-(*s*-Butyltelanyl)-3-penten-2-one (11h). ^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm) 7.16 (q, J=1.2 Hz, 1H); 3.20 (sext., J=7.2 Hz, 1H); 2.48 (d, J=1.2 Hz, 3H); 2.15 (s, 3H); 1.80–1.68 (m, 2H); 1.63 (d, J=7.2 Hz, 3H); 0.98 (t, J=7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 196.3; 152.8; 129.0; 32.3; 29.8; 27.3; 23.8; 21.9; 13.7; LR-MS m/z (rel. int.) 270 (10)(M^+); 213 (53); 83 (34); 57 (100); IR (neat) ν (cm^{-1}) 2958; 2922; 1648; 1528; 1198.

5.2.8. (*Z*)-4-(*t*-Butyltelanyl)-3-penten-2-one (11i). ^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm) 7.08 (q, J=1.2 Hz, 1H); 2.59 (d, J=1.2 Hz, 3H); 2.14 (s, 3H); 1.65 (s, 9H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ (ppm) 196.6; 155.2; 129.7; 35.2; 31.5; 28.5; 14.1; LR-MS m/z (rel. int.) 270 (12)(M^+); 213 (100); 83 (25); 57 (9); IR (neat) ν (cm^{-1}) 2957; 2925; 1647; 1527; 1199.

5.3. Reaction of lithium *n*-butyltellurolate (14a) with enolphosphate (13g). One pot procedure

In a three necked flask under nitrogen equipped with a mechanical stirrer and a dropping funnel was placed a suspension of sodium hydride (0.083 g of a 95% suspension in mineral oil, 3.3 mmol) in THF (2 mL). The mixture was cooled to 0°C and then a solution of the β-keto amide **18** (0.51 g, 3.0 mmol) in THF (2 mL) was added dropwise. After 30 min of stirring diethyl phosphorochloridrate **17** (0.57 g, 3.3 mmol) was added all at once and the reaction mixture was allowed to reach room temperature and stirred for 1 h. To a second flask containing a suspension of elemental tellurium (0.51 g, 4 mmol) in THF (4 mL), *n*-butyllithium (from a 1.4 M solution in hexane, 2.9 mL, 4 mmol) was added. The in situ prepared enolphosphate **13g** was transferred via canula to the resulting clear solution of *n*-BuTeLi. The progress of the reaction was monitored by thin layer chromatography. The reaction was very fast. After a few minutes after the addition of the enolphosphate the mixture was diluted with ethyl acetate (50 mL) and the organic phase was washed with brine (3×50 mL) and then dried with magnesium sulfate. The solvents were evaporated and the residue was purified by column chromatography on silica gel eluting with hexane/ethyl acetate (9/1). The telluride was recrystalized from a mixture of pentane/petroleum ether (15/1).

5.3.1. Morpholine, 4-[1-oxo-3-(butyl tellanyl)-2-butenyl] (11g). ^{1}H NMR ($CDCl_3$, 500 MHz) δ (ppm) 6.89 (q, J=1.2 Hz, 1H); 3.55–3.67 (m, 8H); 2.54 (t, J=7.6 Hz, 2H); 2.41 (d, J=1.2 Hz, 3H); 1.72 (quint., J=7.6 Hz, 2H); 1.41 (sext., J=7.6 Hz, 2H); 0.91 (t, J=7.6 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ (ppm) 166.5; 146.4; 118.0; 66.7; 45.6; 42.2; 33.5; 27.5; 25.3; 13.4; 5.7; ^{125}Te NMR ($CDCl_3$, 157.79 MHz) δ (ppm) 561; LR-MS m/z (rel. int.) 341 (7)(M^+); 284 (100); 154 (24); 114 (14); 86 (45); 57 (24); IR (neat) ν (cm^{-1}) 2957; 2922; 2854; 1607; 1554; 1458; 1441; 1238; 1117; 810; Anal. calcd for $C_{12}H_{21}NO_2Te$: C, 42.53; H, 6.25; Found: C, 42.49; H, 6.14; mp: 69.3°C.

5.4. Reaction of bromomagnesium phenyltellurolate (14d) with the enolphosphate (13a)

In a three necked flask (50 mL) equipped with a reflux condenser, a nitrogen inlet and a dropping funnel was placed activated magnesium (0.8 g, 33 mmol) and THF (10 mL). To this suspension was slowly added via dropping funnel a solution of bromobenzene (4.7 g, 30 mmol) in THF (20 mL). The mixture was heated to 40°C and then the Grignard reagent (10.1 mL, 10.1 mmol) was transferred via syringe to a second three necked flask under nitrogen containing a suspension of elemental tellurium (1.27 g, 10 mmol) in THF (10 mL). The mixture was maintained 1 h under reflux and then cooled to room temperature. The enolphosphate **13a** (1.8 g, 8 mmol) was added and the mixture was stirred for 5 h. Then ethyl acetate (50 mL) was added and the organic phase was washed with brine (3×50 mL), dried with magnesium sulfate and the solvents were evaporated. The residue was purified by silica gel column chromatography eluting with hexane/ethyl acetate (9/1).

5.4.1. (*Z*)-4-(Phenyltelanyl)-3-penten-2-one (11j). ^{1}H NMR ($CDCl_3$, 500 MHz) δ (ppm) 7.89–7.87 (m, 2H); 7.41–7.37 (m, 1H); 7.30–7.27 (m, 2H); 7.25 (quart, J=1.3 Hz, 1H); 2.25 (s, 3H); 2.11 (d, J=1.3 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ (ppm) 196.8; 156.7; 141.1; 129.1; 128.6; 128.1; 119.2; 29.7; 26.0; ^{125}Te NMR ($CDCl_3$, 157.79 MHz) δ (ppm) 879; LR-MS m/z (rel. int.) 290 (48)(M^+); 213 (100); 77 (83); IR (neat) ν (cm^{-1}) 3064; 3043; 1634; 1520; 1429; 1203; 1104; 834; 734; 627; Anal. calcd for $C_{11}H_{12}OTe$: C, 45.90; H, 4.20; Found: C, 45.83; H, 4.01; mp: 104.3°C.

5.5. Reaction of lithium-2-thienyltellurolate (14e) with the enolphosphate (13a)

To a solution of thiophene (0.17 g, 2 mmol) in THF (4 mL) under nitrogen at −78°C was slowly added *n*-butyllithium (from a 1.4 M solution in hexane, 1.6 mL, 2.2 mmol). The cooling bath was removed and the mixture was stirred until the temperature reach 0°C (30 min). Then elemental tellurium (0.23 g, 1.8 mmol) was rapidly added and the mixture was stirred until room temperature was reached

(30 min). To this solution, cooled to 0°C, was added the enolphosphate **13a** (0.35 g, 1.5 mmol) and the mixture was stirred at room temperature for 5 h. Then ethyl acetate (50 mL) was added and the organic phase was washed with brine (3×50 mL). The solvents were evaporated and the residue was purified by silica gel column chromatography eluting with hexane/ethyl acetate (9/1).

5.5.1. (*Z*)-4-[(2-Thienyl)telanyl]-3-penten-2-one (11k). ^{1}H NMR ($CDCl_3$, 500 MHz) δ (ppm) 7.53–7.52 (m, 1H); 7.41–7.40 (m, 1H); 7.30 (d, J=1.2 Hz, 1H); 7.04–7.02 (m, 1H); 2.25 (s, 3H); 2.15 (d, J=1.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ (ppm) 197.2; 159.8; 141.9; 134.5; 128.8; 109.5; 29.4; 27.1; ^{125}Te NMR ($CDCl_3$, 157.79 MHz) δ (ppm) 716; LR-MS m/z (rel. int.): 296 (79)(M^+); 292 (42); 213 (44); 83 (100); 51 (8); IR (neat) ν (cm^{-1}) 3089; 3073; 1638; 1528; 1361; 1211; 1108; 843; 708; 629; Anal. calcd for $C_9H_{10}OSTe$: C, 36.79; H, 3.43; Found: C, 37.19; H, 3.40.

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