Journal of Organometallic Chemistry, 308 (1986) 211–222
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

SYNTHESIS OF VINYLIC TELLURIDES

M.J. DABDOUB, V.B. DABDOUB, J.V. COMASSETO* and N. PETRAGNANI
Instituto de Química, Universidade de São Paulo, Caixa Postal, 20.780, São Paulo, S.P. (Brasil)

(Received November 25th, 1985)

Summary

Synthetic routes to vinylic tellurides employing nucleophilic and electrophilic tellurium species are described. Reaction of vinyl Grignard reagents with organotellurenyl bromides leads to vinylic tellurides (p-$CH_3OC_6H_4TeCH{=}CHC_6H_5$, p-$CH_3OC_6H_4Te(CH_3)C{=}CH_2$, n-$C_4H_9TeCH{=}CH_2$) in 71–86% yield; vinyltellurenyl iodides react with Grignard reagents to give vinylic tellurides (p-$CH_3OC_6H_4$-$Te(CH_3)C{=}CH_2$, p-$CH_3OC_6H_4TeCH{=}CH_2$, n-$C_4H_9TeCH{=}CH_2$) in 64–71% yield; *trans*-β-Bromostyrene react with p-$CH_3OC_6H_4Te^-$ and n-$C_4H_9Te^-$ to give vinylic tellurides of *trans* configuration (p-$CH_3OC_6H_4TeCH{=}CHC_6H_5$, n-$C_4H_9$-$TeCH{=}CHC_6H_5$) in 86 and 83% yield, respectively; reaction of vinyl Grignard reagents with elemental tellurium followed by alkylation with n-bromobutane gives vinylic tellurides (n-$C_4H_9Te(CH_3)C{=}CH_2$, n-$C_4H_9TeCH{=}CH_2$, n-$C_4H_9TeCH{=}CHCH_3$, n-$C_4H_9TeCH{=}CHC_6H_5$) in 73–79% yield; divinyl ditellurides ((C_6H_5-$CH{=}CHTe)_2$, $(CH_3CH{=}CHTe)_2$, $(CH_2{=}CHTe)_2$, $(CH_2{=}C(CH_3)Te_2)$ were prepared in 58–67% yield by reaction of vinyl Grignard reagents with elemental tellurium followed by air oxidation; divinyl ditellurides react with formamidinesulfinic acid in 50% sodium hydroxide under phase transfer conditions in the presence of n-C_4H_9Br to give vinylic tellurides (n-$C_4H_9TeCH{=}CHC_6H_5$, p-$C_4H_9TeCH{=}CHCH_3$, n-$C_4H_9Te(CH_3)C{=}CH_2$, n-$C_4H_9TeCH{=}CH_2$) in 81–86% yield; addition of n-$C_4H_9Te^-$ to acetylenes gives vinylic tellurides of *cis*-configuration (n-C_4H_9-$TeCH{=}CHC_6H_5$, n-$C_4H_9CH{=}CHCH_2\overline{NCH_2CH_2OCH_2CH_2}$, n-$C_4H_9TeCH{=}CHCH_2O\overline{CHOCH_2\text{-}CH_2CH_2CH_2}$) in 78–93% yield.

Introduction

Although organotellurium derivatives have been known since the early 1800's [1], and progress in this field of chemistry is well documented [2–8], the synthetic potential of this class of organoelemental compounds has only recently received the attention of organic chemists [8].

0022-328X/86/$03.50

Vinylic tellurides are among the classes of organotellurium reagents with expected synthetic utility, by analogy with a large range of well established transformations of the similar selenium derivatives. For example, vinylic tellurides were shown to be synthetic equivalents of 1,1-dilithioethene [9] and to react with Grignard reagents [10] and carbon monoxide [11] under transition metal catalysis to give coupling products free of tellurium.

In spite of the many preparative methods described for vinylic selenides [12], no extensive systematic study has been undertaken for the synthesis of analogous tellurium compounds.

The addition of tellurium tetrachloride to phenyl- and diphenyl-acetylene leading to vinylic species of tellurium was described by one of us many years ago [13]. This was the first method developed for the synthesis of vinylaryltellurium tri- and di-chlorides as well as vinyl aryl tellurides and ditellurides. Recently, Uemura et al. [14] extended this reaction to some other acetylenes. A vinyl aryl telluride was also obtained by means of the reaction of β-styrylmagnesium bromide with 2-naphthyltellurenyl iodide [13], which was the only stable tellurenyl halide known at that time.

In a different approach, the addition of the nucleophilic tellurium species Te^{2-} [15–21] and $ArTe^{-}$ [22–25] to acetylenes, specially to acetylenic carbonyl compounds [23–25], has been studied.

Vinyl aryl tellurides were prepared by an exchange reaction of divinylmercury with diaryl ditellurides [26].

In view of our continuous interest in the organic chemistry of tellurium, we have devoted some efforts to the synthesis of vinylic tellurides and we describe in this paper our results.

Results and discussion

In this work we have studied two general routes to vinylic tellurides, employing respectively electrophilic and nucleophilic tellurium species.

A. Starting from electrophilic tellurium species

a. The reaction of aryltellurenyl halides with vinylic Grignard reagents. Some years ago we have observed that in spite of their instability in the solid state, aryltellurenyl halides are stable in solution and react in this form with Grignard reagents giving mixed tellurides [27]. In the present work, we exploited this reaction as a general method for preparing vinylic tellurides starting from the appropriate vinylic Grignard reagents. The reaction was performed by adding a solution of organotellurenyl bromide prepared in situ in benzene/tetrahydrofuran (THF) [27] to the Grignard reagent in THF at 0°C (eq. 1).

$$\mathrm{RCH{=}CR^1MgBr} + [\mathrm{R^2TeBr}] \xrightarrow[0^\circ\mathrm{C},\,\mathrm{N_2}]{\mathrm{THF/benzene}} \mathrm{RCH{=}CR^1TeR^2} \quad (1)$$

$$\begin{pmatrix} R = C_6H_5;\ R^1 = H,\ R^2 = p\text{-}CH_3OC_6H_4; \\ R = H,\ R^1 = CH_3,\ R^2 = p\text{-}CH_3OC_6H_4; \\ R = H,\ R^1 = H,\ R^2 = p\text{-}CH_3OC_6H_4; \\ R = H,\ R^1 = H,\ R^2 = n\text{-}C_4H_9 \end{pmatrix}$$

b. Reaction of vinyltellurenyl iodides wigh Grignard reagents. An alternative approach uses reactions of vinyltellurenyl iodides with Grignard reagents as shown in eq. 2.

$$\mathrm{RCH{=}CR^1TeI + R^2MgX \rightarrow RCH{=}CR^1TeR^2} \qquad (2)$$

$$\begin{aligned}(&\mathrm{R = H, R^1 = CH_3, R^2 = \mathit{p}\text{-}CH_3OC_6H_4;}\\ &\mathrm{R = H, R^1 = H, R^2 = \mathit{p}\text{-}CH_3OC_6H_4;}\\ &\mathrm{R = H, R^1 = H, R^2 = n\text{-}C_4H_9})\end{aligned}$$

The vinyltellurenyl iodides were generated in solution as described previously [27] by reaction of divinyl ditellurides with iodine. Addition of this solution to a solution of the appropriate Grignard reagent in THF gives the vinylic tellurides in good yields.

B. Starting from nucleophilic tellurium species

a. Reaction of organotellurolate anions with trans-β-bromostyrene. Reaction of β-bromostyrene with the *p*-methoxyphenyltellurolate anion generated by the reduction of bis(*p*-methoxyphenyl) ditelluride with lithium aluminium hydride results in the expected vinylic telluride in 86% yield. The reaction was performed in a mixture of THF/hexamethylphosphoric triamide (HMPA), (1/2) and completed after 3 h of stirring at the boiling point (eq. 3). On the other hand, reaction of *trans*-β-bromostyrene with the analogously generated butyltellurolate anion under the same reaction conditions was completed after 15 min of stirring, furnishing the corresponding vinylic telluride in 83% yield (eq. 3). This fact indicates the greater nucleophilicity of the butyltellurolate anion compared with the aromatic analog. In both cases, the resulting vinylic telluride exhibits *trans* stereochemistry as clearly shown by the IR and ^{1}H NMR spectra (Table 1).

$$\mathrm{RTeTeR \xrightarrow[\text{HMPA, r.t.}]{\text{LiAlH}_4\text{/THF}} 2[RTe^-] \xrightarrow[\text{THF, reflux}]{\text{C}_6\text{H}_5\text{CH=CHBr}} \underset{\textit{trans}}{C_6H_5CH{=}CHTeR}} \qquad (3)$$

$$(\mathrm{R = \mathit{p}\text{-}CH_3OC_6H_4;\ n\text{-}C_4H_9})$$

At present, we are unable to determine if the reaction involves an addition–elimination mechanism or a direct nucleophilic substitution at the vinylic carbon.

b. Reaction of bromomagnesium ethene tellurolates with n-bromobutane. Reaction of elemental tellurium with Grignard or organolithium reagents followed by trapping the intermediate bromo-magnesium or -lithium tellurolate with alkyl halides is a well established procedure for the synthesis of mixed tellurides [7]. In the present work this methodology has been successfully applied to the synthesis of vinylic tellurides (eq. 4).

$$\mathrm{RCH{=}CR^1MgBr \xrightarrow[\text{(2) n-C}_4\text{H}_9\text{Br}]{\text{(1) Te/THF, reflux}} RCH{=}CR^1TeC_4H_9\text{-}n} \qquad (4)$$

$$\begin{aligned}(&\mathrm{R = H, R^1 = CH_3;}\\ &\mathrm{R = H, R^1 = H;}\\ &\mathrm{R = CH_3, R^1 = H;}\\ &\mathrm{R = C_6H_5, R^1 = H})\end{aligned}$$

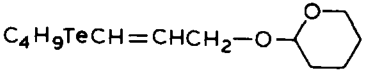
Addition of elemental tellurium to the Grignard reagent in tetrahydrofuran followed by reflux until the complete dissolution of tellurium and subsequent reaction with n-bromobutane led to the vinyl butyl tellurides in good yields.

(Continued on p. 217)

TABLE 1

YIELDS AND PHYSICAL DATA OF THE COMPOUNDS OBTAINED

	Yield (%)	Reaction time (h)	M.p. (°C) or b.p. (°C/mmHg)	IR (cm^{-1})	^1H NMR, (ppm), J(Hz), TMS internal	Analyses (Found (calcd.) (%))	
						H	C
p-$CH_3OC_6H_4TeCH{=}CHC_6H_5$ *trans*	72 [d] 86 [f]	1.0 3.0	68–69 [a]	1570(m) 960(m)	3.81(s, 3H); 6.80 (d, J 9, 2H); 6.93(d, J 16, 1H); 7.26(s, 5H); 7.53(d, J 16, 1H); 7.72(d, J 9, 2H)	53.54 (53.31)	4.21 (4.14)
p-$CH_3OC_6H_4TeCH{=}CHC_6H_5$ *cis*	63 [m]	72	68–69 [a]	1595(m) 755(m)	3.81(s, 3H); 6.82 (d, J 9, 2H); 7.04(d, J 11, 1H); 7.35(m, 5H); 7.45(d, J 11, 1H); 7.74 (d, J 9, 2H)	53.23 (53.31)	4.31 (4.14)
p-$CH_3OC_6H_4TeCH{=}CH_2$	74 [d] 68 [e]	1.0 1.0	83–84/0.5 [b]	1580(m)	3.80(s, 3H); 5.71(d, J 17, 1H); 6.28(d, J 10, 1H); 6.80(d, J 9, 2H); 7.16(dd, J 17, J 10, 1H); 7.69(d, J 9, 2H)	41.15 (41.28)	3.91 (3.82)
p-$CH_3OC_6H_4Te(CH_3)C{=}CH_2$	86 [d] 71 [e]	1.0 1.0	68/0.05 [b]	1575(m)	2.15(dd, J ~ 1.5, J ~ 1, 3H); 3.81 (s, 3H); 5.31(q, J ~ 1, 1H); 5.83 (q, J ~ 1.5, 1H); 6.80(d, J 9, 2H); 7.76(d, J 9, 2H)	43.53 (43.51)	4.79 (4.35)
$C_4H_9TeCH{=}CHC_6H_5$ *trans*	83 [f] 79 [g] 86 [i]	0.25 0.5 0.25	$95/5\times10^{-1}$ [b]	1570(m) 930(m)	0.93(t, J 7, 3H); 1.1–2.1(m, 4H); 2.86(t, J 7, 2H); 6.96 (d, J 7, 1H); 7.33(s, 5H); 7.56(d, J 17, 1H)	49.83 (50.06)	5.28 (5.56)
$C_4H_9TeCH{=}CHC_6H_5$ *cis*	93 [j]	1.7	$105/5\times10^{-3}$ [a]	1590(m) 755(s)	0.93(t, J 7, 3H); 1.1–2.1(m, 4H); 2.76(t, J 7, 2H); 7.00 (d, J 11, 1H); 7.33 (s, 5H); (7.44(d, J 11, 1H)	49.96 (50.06)	5.74 (5.56)
$C_4H_9TeCH{=}CH_2$	71 [d] 64 [e] 76 [g] 82 [i]	1.0 1.0 0.5 0.33	60/4.0 [a]	1585(m)	0.93(t, J 7, 3H); 1.1–2.1(m, 4H); 2.75(t, J 7, 2H); 5.79 (d, J 17, 1H); 6.21(d, J 10, 1H); 7.16(dd, J 17, J 10, 1H)		

$C_4H_9Te(CH_3)C{=}CH_2$	73 [g] 81 [i]	0.5 1.5	52/2.75 [a]	1586(m)	0.93(t, J 7, 3H); 1.1–2.1(m, 4H); 2.25(dd, J ~ 1.5, J ~ 1.0, 3H); 2.80(t, J 7, 2H); 5.38 (q, J ~ 1, 1H); 5.85(q, J ~ 1.5, 1H)		
$C_4H_9TeCH{=}CHCH_3$	77 [g] 84 [i]	0.5 4.0	70/3.75 [a]	1585(m)	0.91(t, J 7, 3H); 1.1–2.1 (m, 7H); 2.68(t, J 7, 2H); 5.9–6.7(m, 2H)		
	78 [j,l]	4.0	96/0.2 [b]	1585(m)	0.91(t, J 7, 3H); 1.1–2.1 (m, 10 H); 2.65(t, J 7, 2H); 3.4–4.4(m, 4H); 4.6(m, 1H); 6.38(dt, J 9, J 5, 1H); 6.82(dt, J 9, J ~ 1.5, 1H)	44.42 (44.22)	6.86 (6.75)
	81 [j,l]	2.0	82/1.0 [b]	1587(m)	0.91(t, J 7, 3H); 1.1–2.1(m, 4H); 2.2–2.7(m, 6H); 2.9(dd, J 5, J ~ 1.5, 2H); 3.5–3.9(m, 4H); 6.31(dt, J 9, J5, 1H); 6.89 (dt, J 9, J 1.5, 1H)	42.40 (42.49) N 4.39 (4.50)	6.89 (6.76)
$(CH_2{=}CHTe)_2$	67 [h]	1.0	[c]	1570(m)	5.85(d, J 17, 2H); 6.13(d, J 10. 2H); 7.10(dd, J 17, J 10, 2H)	16.02 (15.52)	2.00 (1.94)
$CH_2{=}C(CH_3)Te]_2$	64 [h]	1.0	[c]	1610(m)	2.38(dd, J 1.5, J 1, 6H); 5.68 (q, J 1, 2H); 5.80(q, J ~ 1.5, 2H)	21.61 (21.35)	2.99 (2.96)
$(CH_3CH{=}CHTe)_2$	61 [h]	1.0	[c]	1600(m)	1.85(dd, J 7, J ~ 1.5, 6H); 5.95 (dq, J 9, J 7, 2H)	21.74 (21.35)	3.05 (2.96)
$(C_6H_5CH{=}CHTe)_2$	58 [h]	1.0	[c]	---	7.3(m)		
$C_4H_9Te(Cl)_2CH{=}CH_2$ [n]	[o]	[p]	[c]	1590(w)	1.01(t, J 7, 3H); 1.54(sext., J 7, 2H); 1.95(quint., J 7, 2 H); 6.63(d, J 17, 1H); 6.70(d, J 7, 1H); 7.20(dd, J 17, J 7, 1 H)	25.55 (25.47)	4.16 (4.24)
$C_4H_9Te(Cl)_2(CH_3)C{=}CH_2$ [n]	[o]	[p]	[c]	1618(w)	1.03(t, J 7, 3H); 1.58(sext., J 7, 2H); 2.21(quint., J 7, 2H); 2.5(m, 3H); 3.63(t, J 7, 2 H); 6.08(m, 2H)	27.93 (28.32)	4.60 (4.72)

	Yield (%)	Reaction time (h)	M.p. (°C) or b.p. (°C/mmHg)	IR (cm^{-1})	^1H NMR, (ppm), *J*(Hz), TMS internal	Analyses (Found (calcd.) (%))	
						H	C
$C_4H_9Te(Cl)_2CH{=}CHCH_3$ [n]	[o]	[p]	[c]	1610(m)	1.00(t, *J* 7, 3H); 1.55(sext., *J* 7, 2H); 1.9–2.6 (m, 2H); 2.18 (dd, *J* 7, *J* ~ 1, 3H); 3.66(t, *J* 7, 2H); 6.53(dq, *J* 9, *J* 7, 1H); 7.20(dq, *J* 9, *J* 1, 1H)	28.23 (28.32)	4.58 (4.72)
$C_4H_9Te(Cl)_2CH{=}CHC_6H_5$ [n]	[o]	[p]	[c]	1575(m)	1.00(t, *J* 7, 3H); 1.53(sext., *J* 7, 2H); 2.16 (quint., *J* 7, 2H); 3.58(t, *J* 7, 2H); 7.26(d, *J* 16, 1H); 7.45(m, 5H); 7.86 (d, *J* 16, 1H)	40.03 (40.15)	4.43 (4.46)

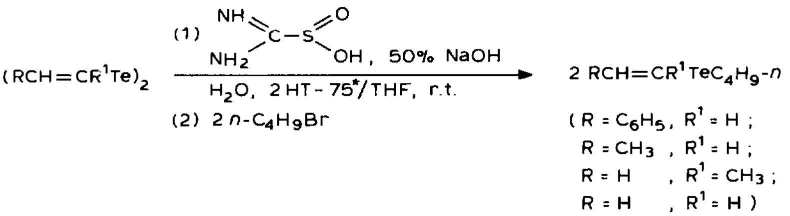
[a] Distilled in short path. [b] Distilled in kugelrohrofen. [c] Purified by column chromatography. [d] Prepared from reaction of vinyl Grignard reagents with organotellurenyl bromides. [e] Prepared from reaction of vinyltellurenyl iodides with Grignard reagents. [f] Prepared from reaction of *trans*-β-bromostyrene with organotellurolates. [g] Prepared from reaction of vinylic Grignard reagents with elemental tellurium followed by alkylation. [h] Prepared from reaction of vinylic Grignard reagents with elemental tellurium followed by oxidation. [i] Prepared from divinyl ditellurides under phase transfer conditions. [j] Prepared from addition of n-butyltellurolate to acetylenes. [l] Yield of the distilled product. Analytically pure samples were obtained from preparative thin layer chromatography. [m] Prepared from addition of *p*-methoxyphenyltellurolate to phenyl acetylene under phase transfer conditions. [n] Prepared by treating the vinylic tellurides with excess sulfuryl chloride. [o] Quantitative yield. [p] The reaction is immediate at room temperature.

If the intermediate bromomagnesium ethenetellurolates, instead of being treated with n-bromobutane, are treated with water at 0°C and then stirred in the presence of air, divinyl ditellurides are formed (eq. 5). Divinyl ditellurides are very poorly described compounds [13].

$$2RCH{=}CR^1TeMgBr \xrightarrow[NH_4Cl]{H_2O,\,0°C} 2[RCH{=}CR^1TeH] \overset{air}{\rightarrow} (RCH{=}CR^1Te)_2 \qquad (5)$$

$$\begin{pmatrix} R = C_6H_5;\ R^1 = H; \\ R = CH_3;\ R^1 = H; \\ R = H;\ R^1 = H; \\ R = H;\ R^1 = CH_3 \end{pmatrix}$$

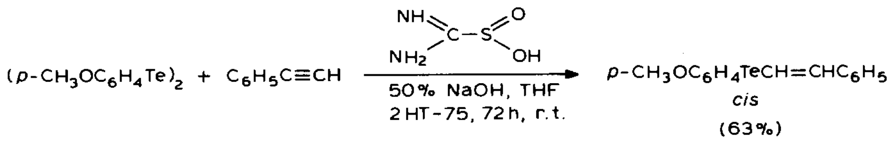
A general method of synthesis of alkyl- and aryl-chalcogenate anions from diorganodichalcogenides using formamidinesulfinic acid (thiourea dioxide) in 50% sodium hydroxide in the presence of a phase transfer catalyst as the reducing system was recently developed in our laboratory. Trapping of the intermediate organochalcogenate anions with alkyl and aryl halides leads to the corresponding organic chalcogenides in high yield [28]. This methodology was now used for the synthesis of vinylic tellurides (eq. 6).



(6)

The reaction was performed simply by stirring the mixture of reagents and substrates at room temperature for the time indicated in Table 1. Separation of the phases and normal work-up lead to the vinyl butyl tellurides in high yields.

c. *Addition of organotellurolate anions to acetylenes.* The above described phase transfer technique was used to prepare *p*-methoxyphenylstyryl telluride through the reaction of bis(*p*-methoxyphenyl) ditelluride and phenyl acetylene in THF in the presence of formamidine sulfinic acid, 50% sodium hydroxide and catalytic amount of 2HT-75 [29]. *p*-Methoxyphenylstyryl telluride of *cis* configuration was obtained in 63% yield after 72 h stirring at room temperature (eq. 7).



(7)

On the other hand, reaction of acetylenes with the butyltellurolate anion generated by reduction of dibutyl ditelluride with sodium borohydride in ethanol for the

---

[*] A trade name for a mixture of dialkyldimethylammonium chlorides (85% n-C_{18} and 15% n-C_{16}) [29].

time indicated in Table 1 leads to the corresponding vinylic telluride of *cis* configuration in good yields (eq. 8).

$$\mathrm{RC{\equiv}CH + (n\text{-}C_4H_9Te)_2 \xrightarrow[\text{reflux}]{NaBH_4/EtOH} \underset{\textit{cis}}{RCH{=}CHTeC_4H_9\text{-}n}} \qquad (8)$$

$$\mathrm{(R = C_6H_5,\ CH_2O\overline{CHOCH_2CH_2CH_2C}H_2,\ CH_2\overline{NCH_2CH_2OCH_2C}H_2)}$$

C. Attempts to prepare vinylic tellurides by reduction of the carbon–carbon triple bond of telluroacetylenes

The reduction of the carbon–carbon triple bond of acetylenic tellurides was attempted using many reducing agents. However, instead of the expected vinylic telluride the tellurium free phenyl actylene and the corresponding bis(*p*-methoxyphenyl) ditelluride or di-n-butyl ditelluride were obtained in high yields (eq. 9).

$$\mathrm{C_6H_5C{\equiv}CTeR^1 \xrightarrow{[H]} C_6H_5C{\equiv}CH + (R^1Te)_2} \qquad (9)$$

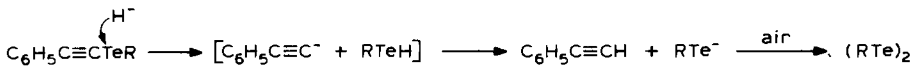
$$\left(\begin{array}{l}\mathrm{R^1 = n\text{-}C_4H_9,\ 96\%,}\\ \mathrm{R^1 = \mathit{p}\text{-}CH_3OC_6H_4,\ 95\%)}\end{array}\right)$$

$$\mathrm{([H] = NaBH_4,\ LiAlH_4,\ N_2H_4/NaOH,\ BH_3)}$$

Addition of n-bromobutane to the reaction mixture prior to the oxidation step leads to the formation of phenyl acetylene and di-n-butyltelluride in 89% yield (eq. 10).

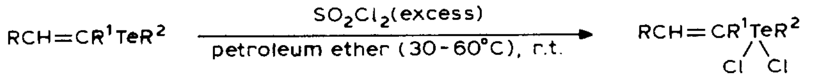
$$\mathrm{C_6H_5C{\equiv}CTeC_4H_9\text{-}n \xrightarrow[\text{(2) n-C}_4\text{H}_9\text{Br, 10 min}]{\text{(1) NaBH}_4\text{/EtOH, r.t.}} \underset{(89\%)}{(n\text{-}C_4H_9)_2Te} + C_6H_5C{\equiv}CH} \qquad (10)$$

This last result indicates that the reaction involves the intermediate formation of an alkanetellurolate anion as depicted below.



Presently we are investigating the reduction of telluroacetylenes as a general method of synthesis of dialkyl ditellurides and dialkyl tellurides.

The aliphatic vinylic tellurides prepared in this work are volatile compounds of unpleasant smell. The elemental analyses were then performed with the corresponding vinylic tellurium dichlorides, which were prepared by treating the vinylic tellurides with excess of sulfuryl chloride (eq. 11).



$$\mathrm{RCH{=}CR^1TeR^2 \xrightarrow[\text{petroleum ether (30-60°C), r.t.}]{SO_2Cl_2(excess)} RCH{=}CR^1\underset{Cl\ \ Cl}{Te}R^2} \qquad (11)$$

The vinylic tellurium dichlorides were obtained as colorless oils in quantitative yields.

Experimental

^{1}H NMR spectra were recorded on a Varian T-60 spectrometer in CCl_4 or $CDCl_3$ solutions with Me_4Si as internal standard; IR spectra of films in NaCl were obtained with a Perkin–Elmer 457A spectrophotometer. All the alkyl halides were distilled prior to use. Merck Silica Gel 60 (70–230 mesh and 230–400 mesh) was used for column chromatography and prepared plates (silica gel 60 F_{254} on aluminium) for thin layer chromatography. Melting points were determined in a Kofler hot plate and are uncorrected. 2HT-75 was supplied by Herga Industria Químicas S/A, Rio de Janeiro, Brasil [29]. Bis(*p*-methoxyphenyl) ditelluride was prepared according to published procedures [30]. The Grignard reagents used in this work were freshly prepared by reaction of the appropriate organic halide with magnesium in dry THF [31].

Vinylic tellurides from reaction of vinyl Grignard reagents with organotellurenyl bromides

A solution of the organotellurenyl bromide, prepared by adding 0.40 g (2.5 mmol) of bromine in benzene (5.0 ml) to 2.5 mmol of the corresponding ditelluride in THF (10 ml) (0°C, N_2 atmosphere), was added dropwise (0°C, N_2 atmosphere) to a solution of the Grignard reagent (7.0 mmol) in THF (10 ml). A gradual disappearance of the red color of the reaction mixture was observed. After 1 h of stirring at 0°C, the THF was evaporated and the residue was treated with a saturated solution of ammonium chloride, extracted with ether, dried with $MgSO_4$ and evaporated. The products were purified by column chromatography using hexane/benzene (9/1) as the eluent (the yields and the physical data are summarized in Table 1).

Vinylic tellurides from reaction of trans-β-bromostyrene with organotellurolate anions

A solution of the ditelluride (2.0 mmol) and *trans*-β-bromostyrene (0.73 g, 4.0 mmol) in THF/HMPA (2/8, 10 ml) was added dropwise at room temperature (N_2 atmosphere) to a 50 ml round bottomed flask containing $LiAlH_4$ (0.17 g, 4.5 mmol) in THF (2.0 ml). The dark red color of the ditelluride disappeared at once. The resulting pale green solution was refluxed for the time indicated in Table 1. After cooling to room temperature the reaction mixture was treated with water (1.0 ml) and 10% NaOH (1.0 ml) and then extracted with ether. The ether extract was washed with saturated sodium chloride solution, dried with $MgSO_4$ and evaporated. The residue was purified by recrystallization or by Kugelrohr distillation (Table 1).

Vinylic tellurides from reaction of vinylic Grignard reagents with elemental tellurium followed by alkylation

Elemental tellurium (0.6 g, 5.0 mmol) was added, to a solution of the vinylmagnesium bromide (5.5 mmol) in THF (10 ml) (N_2 atmosphere) under reflux and the reflux maintained for 20 min. The mixture was allowed to reach room temperature and then treated with n-bromobutane (0.7 g, 5.0 mmol). After 10 min of stirring the reaction mixture was cooled to 0°C and treated dropwise with a saturated solution of ammonium chloride, extracted with ether, dried with $MgSO_4$ and the solvent evaporated. Short path distillation of the residue under vacuum afforded the vinyl alkyl tellurides as yellow liquids (The yields and the physical data are in Table 1).

Divinyl ditellurides from reaction of vinylic Grignard reagents with elemental tellurium followed by oxidation

Solutions of bromomagnesium ethenetellurolate (10 mmol) prepared as described above were treated with water at 0°C. After stirring the mixture for 1 h in the presence of air, the phases were separated and the organic layer was dried with $MgSO_4$ and evaporated. The residue was purified by column flash chromatography using hexane as eluent. The divinyl ditellurides were obtained as red oils. Attempts to distil led to decomposition (For yields and physical data see Table 1).

Vinylic tellurides from reaction of vinyl tellurenyl iodides with Grignard reagents

A solution of the vinyltellurenyl iodide, prepared by adding iodine (0.25 g, 1.0 mmol) in benzene to the corresponding divinyl ditelluride (1.0 mmol) in THF (5.0 ml) (0°C; N_2 atmosphere), was added dropwise to a solution of the Grignard reagent in THF (10 ml) at 0°C. A gradual disappearance of the dark red color of the reaction mixture was observed. After the fading of the red color, the mixture was stirred for 1 h at room temperature, treated with a saturated solution of ammonium chloride, extracted with ether, dried with $MgSO_4$ and then the solvent was evaporated. The residue was purified by column chromatography using petroleum ether (30–60°C) ethyl acetate (9/1) as eluent (For yields and physical data see Table 1).

Vinylic tellurides from reaction of bis-vinyl ditellurides with alkyl halides under phase transfer conditions

Formamidinesulfinic acid (0.11 g, 1.0 mmol), n-bromobutane (0.10 g, 2.0 mmol), 2HT-75 [29] (30 mg), and a 50% sodium hydroxyde solution (7.5 ml) was added to a solution of the divinyl ditelluride (1.0 mmol) in THF (7.5 ml) (N_2 atmosphere). The reaction mixture was vigorously stirred at room temperature for the time indicated in Table 1. The phases were separated, the aqueous phase was extracted with ether and the combined organic phases were dried with $MgSO_4$ and evaporated. The residue was purified by column chromatography using hexane as eluent. (For yields and physical data see Table 1).

Addition of p-methoxyphenyltellurolate to phenylacetylene under phase transfer conditions

Formamidesulfinic acid (0.11 g, 1.0 mmol), phenyl acetylene (0.204 g, 2 mmol) 2HT-75 [29] (30 mg), and a 50% sodium hydroxide solution (7.5 ml) was added to a solution of bis(*p*-methoxyphenyl) ditelluride (0.47 g, 1.0 mmol) in THF (7.5 ml) (N_2 atmosphere). The mixture was vigorously stirred under reflux for 72 h. The phases were separated and the aqueous phase was extracted with ether. The combined organic phases were dried with $MgSO_4$ and evaporated. The residue was purified by column chromatography using hexane/benzene (9/1) as the eluent. The product was recrystallized form ethanol. Yield: 0.40 g (63%), m.p. 68–69°C.

Addition of n-butyl tellurolate to acetylenes in ethanol

$NaBH_4$ (0.09 g, 2.5 mmol) was added portionwise to a solution of di-n-butyl ditelluride (0.37 g, 1.0 mmol) and the acetylene (2.0 mmol) in ethanol (6.0 ml) (room temperature, N_2 atmosphere). The red color of the reaction mixture disappeared by the end of the addition. The reaction mixture was stirred under reflux for the time indicated in Table 1. After cooling the mixture to room temperature, water (0.5 ml) and 10% sodium hydroxide solution (0.5 ml) were added. The resulting yellow solution was diluted with ether, washed with a saturated sodium chloride solution, dried with $MgSO_4$ and evaporated. The residue was distilled in a kugelrohrofen under vacuum (for yields, reaction time and physical data see Table 1).

Preparation of butyl(tellurophenyl)acetylene

n-Butyllithium (1.35 *M* in hexane) (22.2 ml, 30 mmol) was added to a solution of phenylacetylene (3.1 g, 30 mmol) in THF (15 ml) (0°C, N_2 atmosphere). After 5 min of stirring at 0°C, elemental tellurium (3.9 g, 30 mmol) was added and the mixture was refluxed until the complete disappearance of the tellurium (~ 30 min). The heating was then removed and n-bromobutane (4.10 g, 30 mmol) was added. The stirring was continued for 40 min at room temperature and the resulting mixture was diluted with ether (60 ml) washed with saturated sodium chloride solution, dried with $MgSO_4$ and evaporated. The residue was distilled in a kugelrohrofen under vacuum. Yield: 8.31 g (97%). IR: 2020, 1585 cm^{-1}. ^1H NMR (CCl_4): δ 0.96 (t, J 7 Hz, 3H), 1.1–2.2 (m, 4H), 2.91 (t, J 7 Hz, 2H), 7.36 (m, 5H), Found: C, 50.26; H, 4.98; $C_{12}H_{14}Te$ calcd.: C, 50.42; H, 4.90%.

Preparation of phenyl(p-methoxyphenyltelluro)acetylene

To a solution of lithium phenylacetylide prepared as described above was added a solution of *p*-methoxyphenyltellurenyl bromide, prepared by adding 1.60 g (10 mmol) of bromine in benzene (5 ml) to 4.69 g (10 mmol) of bis (*p*-methoxyphenyl) ditelluride in THF (10 ml) (0°C, N_2 atmosphere). Work-up as described above afforded phenyl(*p*-methoxyphenyltelluro)acetylene. Recrystallization from $CHCl_3$/petroleum ether gave 4.90 g (73%). m.p. 71–72°C. Found: C, 55.4; H, 3.72. $C_{15}H_{13}OTe$ calcd.: C, 53.63; H, 3.57%. ^1H NMR ($CDCl_3$): 3.7 (s, 3H), 6.79 (d, J 9 Hz, 2H), 7.3 (m, 5H), 7.71 (d, J 9 Hz, 2H).

Ditellurides from organo(tellurophenyl)acetylenes

$NaBH_4$ (0.074 g, 2.0 mmol) in ethanol (3.0 ml) was added to a solution of the organotelluroacetylene (2.0 mmol) in ethanol (30 ml). The pale yellow solution turned immediately dark red. After 10 min of stirring at room temperature the mixture was cooled to 0°C, water (0.5 ml) and 10% sodium hydroxide solution were added and the mixture was stirred at room temperature for 5 min. The reaction mixture was then diluted with ether (30 ml), washed with a saturated sodium chloride solution, dried with $MgSO_4$, the solvents were removed and the residue chromatographed on siliga gel (eluting with hexane).

Di-n-butyltelluride from butyl(tellurophenyl)acetylene

A solution of n-butyl(tellurophenyl)acetylene (0.57 g, 2.0 mmol) in ethanol (3.0 ml) (N_2 atmosphere, room temperature) was treated dropwise with $NaBH_4$ (0.074 g, 2.0 mmol) in ethanol (3.0 ml). The mixture was stirred until the red color changed to pale yellow (15 min), then n-bromobutane (0.28 g, 2.0 mmol) was added and the mixture was stirred at room temperature for 10 min. The mixture was then treated with water (0.5 ml), 10% sodium hydroxide solution (0.5 ml), diluted with ether (30 ml), washed with a saturated sodium chloride solution and evaporated in vacuum. The residue was chromatographed on silica gel eluting with hexane. Yield: 0.66 g (89%). ^1H NMR (CCl_4): δ 0.93 (t, J 7 Hz, 6H), 1.1–2.0 (m, 8H), 3.13 (t, J 7 Hz, 4H). Found: C, 25.95; H, 4.87. $C_8H_{18}Te_2$ calcd.: C, 26.00; H, 4.87%.

Preparation of vinyltellurium dichlorides

SO_2Cl_2 was added dropwise to a solution of the vinylic telluride (1.0 mmol) in petroleum ether (30–60°C, 2.0 ml) (caution exothermic reaction) until the discharge of the yellow color. Then the solvent was evaporated and the excess SO_2Cl_2 removed in an oil pump vacuum. The residue was filtered on silica gel eluting with ethyl acetate to give the pure vinyltellurium dichlorides as colorless oils in quantitative yield (for physical data see Table 1).

Acknowledgements

The authors aknowledge the following Brazilian agencies for financial support: FAPESP, CNPq, CAPES and FINEP, M.J. D. acknowledges FAPESP and CNPq for Master fellowships. Acknowledgements are also made to Dra. Riva Moscovici (IQ-USP) for the elemental analyses.

References

1 F. Wöhler, Ann., 35 (1840) 111.
2 H. Rheinboldt, in Houben-Weyl, Methoden der Organischen Chemie, vol. 9, Thieme Stuttgart, 1955.
3 R.A. Zingaro and K.J. Irgolic, in W.C. Cooper (Ed.), Tellurium, Von Nostrand Reinhold, New York, 1971.
4 K.J. Irgolic and R.A. Zingaro, E. Becker and M. Tsutsui (Eds.), Organometallic Reactions, New York, 2 (1975) 117.
5 K.J. Irgolic, The Organic Chemistry of Tellurium, Gordon and Breach, New York, 1974.
6 K.J. Irgolic, J. Organomet. Chem., 103 (1975) 91; 158 (1978) 235; 158 (1978) 267; 189 (1980) 65.
7 N. Petragnani and J.V. Comasseto, F.J. Berry and W.R. McWhinnie (Eds.), Proc. Fourth Intl. Conf. Org. Chem of Selenium and Tellurium, The University of Aston in Birmingham, 1983, p. 99.
8 For review see N. Petragnani and J.V. Comasseto, Synthesis, (1986) 1.
9 T. Kauffmann and H. Allers, Chem. Ber., 116 (1983) 1001.
10 S. Uemura, S. Fukuzawa and S.R. Patil, J. Organomet. Chem., 243 (1983) 9.
11 S. Uemura, K. Ohe, J.R. Kim, K. Kudo and N. Sugita, J. Chem. Soc. Chem. Commun., (1985) 271.
12 J.V. Comasseto, J. Organomet. Chem., 253 (1983) 131.
13 M. Moura Campos and N. Petragnani, Tetrahedron, 18 (1962) 527.
14 S. Uemura, H. Miyoshi and M. Okano, Chem. Lett., (1979) 1357.
15 W. Lohner and K. Praefke, Chem. Ber., 111 (1978) 3745.
16 B.A. Trofimov, A.A. Tatarinova, N.K. Negovskaya and V.M. Bzhevovskii, Zhur. Org. Khim., 18 (1982) 2459.
17 B.A. Trofimov, J. Org. Chem. (USSR), 13 (1977) 456.
18 B.A. Trofimov, V. Vitkovskii, G.K. Musorin, S.V. Amosova and V.V. Keiko, J. Gen. Chem. (USSR), 49 (1979) 345.
19 A. Ulman, J. Manassen, F. Frolow and D. Rabinovich, Tetrahedron Lett., (1978) 1885.
20 J. Meijers, P. Veermeer, D.D. Verkruijsse and C. Brandsma, Recl. Trav. Chim. Pays-Bas, 92 (1973) 1326.
21 A. Zilverschoon, J. Meijers and L. Brandsma, Recl. Trav. Chim. Pays-Bas, 97 (1975) 163.
22 M.R. Detty, B.J. Murray, M.D. Seidler, J. Org. Chem., 47 (1982) 1968.
23 S.R. Buzilova, L.I. Vereshchagin, I.D. Sadekov and V.I. Minkin, Zhur. Obshch. Khim., 46 (1976) 932.
24 S.R. Buzilova, I.D. Sadekov, T.V. Lipovich, T.M. Filippova and L.I. Vereshchagin, Zhur. Obsch. Khim., 47 (1977) 1999.
25 M.R. Detty, B.J. Murray, D.L. Smith and N. Zumbulyadis, J. Am. Chem. Soc., 105 (1983) 875.
26 T.I. Vychkova, G.A. Kalabin and D.F. Kushnarev, J. Org. Chem. (USSR), 17 (1981) 1179.
27 N. Petragnani, L. Torres and K.J. Wynne, J. Organomet. Chem., 92 (1975) 185.
28 J.T.B. Ferreira, J.V. Comasseto, F. Simonelli, E.S. Lang and V.R. Correia, Synthetic Commun., submitted.
29 I.M. Cuccovia, R.M.V. Aleixo, R.A. Mostara, B. Berci Filho, J.B.S. Bonilha, F.H. Quina and H. Chaimovich, Tetrahedron Lett., (1979) 3065.
30 L. Reichel and E. Kirschbaum, Chem. Ber., 76 (1943) 115.
31 L.F. Fieser and M. Fieser, Reagents for Organic Synthesis, John Wiley and Sons, Inc., New York, 1967, p. 415.