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Divinyl ditellurides: synthesis and reactivity

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Abstract

Reaction of vinyl Grignard reagents with elemental tellurium followed by air oxidation furnished divinyl ditellurides [$(CH_2{=}CHTe)_2$, $(CH_2{=}C(CH_3)Te)_2$, $(CH_3CH{=}CHTe)_2$, $(C_6H_5CH{=}CHTe)_2$] in 58–68% yield. When the intermediate bromomagnesium ethenetellurolates were hydrolysed prior to the oxidation, a complex mixture of products was obtained. Divinyl ditellurides were reduced with sodium borohydride in ethanol to give dialkyl ditellurides {$(CH_3CH_2Te)_2$, $[(CH_3)_2CHTe]_2$, $(CH_3CH_2CH_2Te)_2$} in 67–83% yield. When the reduction of di(propen-2-yl) ditelluride was performed in the presence of phenylacetylene, the isopropyl-2-phenylethenyl telluride was obtained in 86% yield, indicating that an alkanetellurolate is an intermediate in this reaction. Contrary to this result, reduction of divinyl ditellurides with lithium aluminum hydride in tetrahydrofuran or with lithium in liquid ammonia furnished ethenetellurolate anions, which on reaction with alkyl halides afforded vinyl alkyl tellurides [$C_4H_9TeCH{=}CH_2$, $C_4H_9Te(CH_3)C{=}CH_2$, $C_4H_9TeCH{=}CHCH_3$] in 63–85% yield.

Introduction

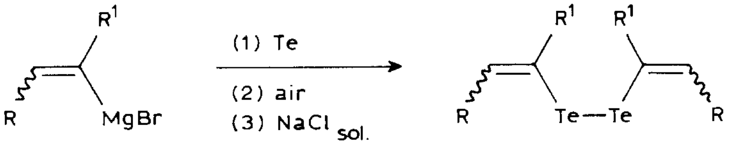
Few divinyl ditellurides are reported in the literature. The first divinyl ditelluride was prepared by reduction of 2-chloro-1,2-diphenylvinyltellurium trichloride with hydrated sodium sulfide [1]. Recently we obtained divinyl, bis(1-methylvinyl), bis(2-methylvinyl) and bis(2-phenylvinyl) ditellurides by treating elemental tellurium with vinylmagnesium bromides and air oxidation of the resulting ethenetellurolates [2].

Tellurium inserts easily into a C_{sp^2}–Mg bond [2–4] but only with difficulty into a C_{sp^3}–Mg bond [4,5].

This paper describes in detail the reaction of vinylmagnesium bromides with elemental tellurium, and the preparation of divinyl ditellurides on a 0.1 molar scale and reports some of the properties of divinyl ditellurides.

Results and discussion

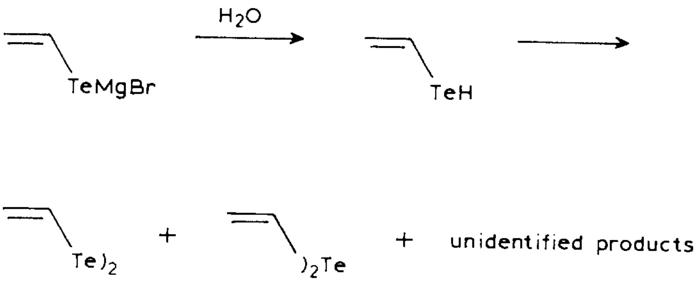
The yields of divinyl ditellurides in the 0.1 molar scale preparations were similar to those obtained in small-scale preparations (eq. 1), when the intermediate ethenetellurolates were oxidized prior to hydrolysis of the reaction mixtures. In some cases the divinyl ditellurides were contaminated by small amounts of divinyl tellurides. The divinyl ditellurides were purified by silica gel flash chromatography. When using hexane as eluent, the chromatography must be done as rapidly as possible (about 5 min) to avoid extensive deposition of elemental tellurium. On the other hand, when carbon tetrachloride was used, no deposition of elemental tellurium was observed.



(1)

	Yield (%)
$R = H$; $R^1 = H$	67
$R = H$; $R^1 = CH_3$	68
$R = CH_3$; $R^1 = H$	61
$R = Ph$; $R^1 = H$	58

If the reaction mixture is hydrolyzed prior to oxidation, a complex mixture of products containing divinyl ditelluride, divinyl telluride, elemental tellurium, and several other products without olefinic protons or olefinic carbons, was obtained (eq. 2).

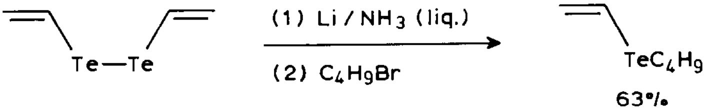


(2)

The products of eq. 2 were obtained in variable ratios from different preparations, probably as a function of the difference in the amount of air accidentally introduced in the system during the hydrolysis process. We interpreted the formation of products without olefinic protons or olefinic carbon in terms of the intermediate formation of a tellurol which could act as a reducing agent promoting undesired side reactions. In this work further evidence for this assumption was obtained.

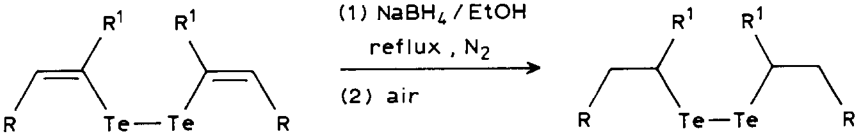
The divinyl ditellurides were reduced with thiourea dioxide in 50% sodium hydroxide solution in a two phase system under catalysis of an ammonium salt leading to the corresponding ethenetellurolate anions which react in situ with alkyl halides to give alkyl vinyl tellurides in high yields [2].

Reduction of divinyl ditelluride with lithium in liquid ammonia leads to lithium ethenetellurolate which was allowed to react with butyl bromide to give butyl vinyl telluride (eq. 3).



(3)

When divinyl ditellurides were reduced with sodium borohydride in ethanol, dialkyl ditellurides were isolated in good yields (eq. 4). When divinyl ditellurides contaminated with the corresponding divinyl tellurides were treated with sodium borohydride only the carbon–carbon double bonds of the divinyl ditellurides were reduced. The divinyl tellurides were recovered unchanged.



(4)

Table 1

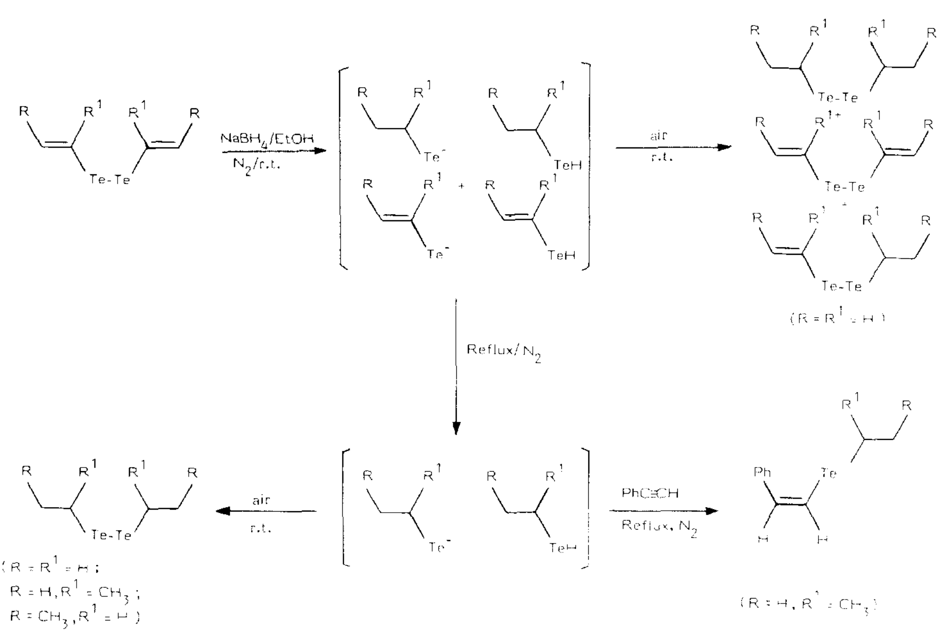
Dialkyl ditellurides by reduction of divinyl ditellurides with sodium borohydride

R	R^1	Yield (%)	Reaction time (min)	^{1}H NMR (δ, ppm; J, Hz)
H	H	83	15	1.60 (t, J 7, 6 H); 2.93 (q, J 7, 4H)
H	CH_3	70	15	1.63 (d, J 7, 12H); 3.41 (hept., J 7, 2H)
CH_3	H	67	105 [a]	1.00 (t, J 7, 6H); 1.78 (sext., J 7, 4H); 3.08 (t, J 7, 4H)

[a] After 45 min reflux an additional amount (0.04 g, 2 mmol) of $NaBH_4$ was added. The mixture was then refluxed for an additional 1 h.

The reduction of carbon–carbon double bonds by sodium borohydride is not a common reaction. It normally requires a strong electron-attracting group on one of the olefinic carbon atoms to take place [6]. Since tellurium is not a strong electron-attracting atom, and because vinylic tellurides are not reduced by sodium borohydride, we presumed that in the present case the reducing agent is not sodium borohydride itself, but an intermediate tellurol formed by reduction of the divinyl ditelluride followed by equilibration with the protic solvent. When the reduction was performed at room temperature and the reaction mixture oxidized with air, divinyl, dialkyl and alkyl vinyl ditellurides were obtained. These compounds are formed by oxidation of alkane- and ethene-tellurolates or -tellurols (Scheme 1).

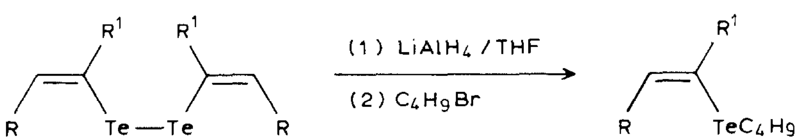
When the reduction was performed in refluxing ethanol, the divinyl ditellurides were completely transformed into dialkyl ditellurides. Under these conditions the



Scheme 1

divinyl ditellurides were completely reduced to the alkanetellurolates, which were oxidized by air to the dialkyl ditellurides. Evidence for the presence of alkanetellurolates in the reaction mixtures was obtained, when phenylacetylene was added to the refluxing reaction mixture prior to oxidation. As expected [2] a *cis*-alkyl vinyl telluride was obtained as the only product (Scheme 1).

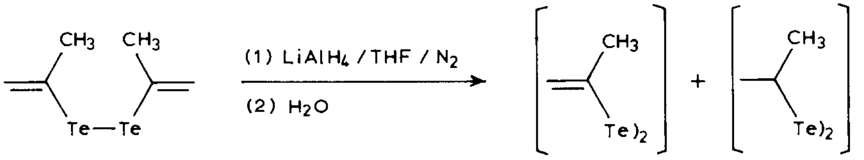
When divinyl ditellurides were treated under nitrogen with lithium aluminum hydride in tetrahydrofuran at room temperature and an alkyl halide was added to the reaction mixture, the alkyl vinyl tellurides were formed in good yields as the only products. The double bond was not reduced (eq. 5).



(5)

	Yield (%)
R = H ; R^1 = CH$_3$	85
R = CH$_3$; R^1 = H	82

However, when the reaction mixture was treated with water under nitrogen and then oxidized with air, a mixture of divinyl ditelluride (20%) and dialkyl ditelluride (69%) was obtained (yield calculated by ^{1}H NMR). These results suggest, that the lithium ethenetellurolate was transformed into the tellurol, which reduced the double bond to give the alkyltellurolate (or tellurol); oxidation of these intermediates gave the observed products (eq. 6).



(6)

Experimental

^1H NMR spectra were recorded on a Varian T-60 spectrometer in CCl_4 or $CDCl_3$ solutions with Me_4Si as internal standard. Merck silica gel 60 (70–230 mesh and 230–400 mesh) was used for column chromatography and prepared plates (silica gel 60 F254 on aluminum) for thin layer chromatography. The Grignard reagents used in this work were prepared prior to use by reaction of the appropriate organic halide with magnesium in dry THF [7]. The THF was distilled from $LiAlH_4$ prior to use. Tellurium of ca. 320 mesh from different suppliers was used. It was dried overnight at 110 °C prior to use.

Divinyl ditellurides

Elemental tellurium (12.7 g, 100 mmol) was added all at once to a 250 ml three-necked round bottomed-flask containing a stirred solution of the vinyl magnesium bromide (110 mmol) in THF (150 ml) under nitrogen. The mixture was refluxed for 30 min under stirring, allowed to reach room temperature, the flask was opened and then the mixture was stirred for 1 h in the presence of air (air was not bubbled through the solution; deposition of some elemental tellurium was observed during the oxidation process). The mixture was treated with a saturated aqueous solution of sodium chloride. The ditelluride was extracted with diethyl ether (3 × 50 ml). The organic layer was dried over anhydrous magnesium sulfate and filtered. The filtrated was evaporated under vacuum. The residue was divided into two portions and purified by flash chromatography on a silica gel column (Ø 2.5 cm, 230–400 mesh, 40 g for each portion) with carbon tetrachloride as eluent. The divinyl ditellurides were obtained as red oils and stored in the dark under refrigeration.

$(CH_2{=}CHTe)_2$. Yield: 10.35 g (67%) IR (film): ν 1570 (m) cm^{-1}. ^1H NMR (CCl_4): δ (ppm) 5.85 (d, *J* 17 Hz, 2H); 6.13 (d, *J* 10 Hz, 2H); 7.10 (dd, *J* 17, *J* 10, 2H).

$[CH_2{=}CH(CH_3)Te]_2$. Yield: 11.46 g (68%). IR (film): ν 1610 (m) cm^{-1}. ^1H NMR (CCl_4): δ (ppm) 2.38 (dd, *J* 15 Hz, *J* 1 Hz, 6H); 5.68 (q, *J* 1 Hz, 2H); 5.80 (q, *J* ~ 1.5 Hz, 2H).

$(CH_3CH{=}CHTe)_2$. Yield: 10.25 g (61%). IR (film): ν 1600 (m) cm^{-1}. ^1H NMR (CCl_4): δ (ppm) 1.85 (dd, *J* 7 Hz, *J* ~ 1.5 Hz, 6H); 5.95 (dq, *J* 9 Hz, *J* 7 Hz, 2H).

$(PhCH{=}CHTe)_2$. Yield: 13.38 g (58%). IR (film): ν 1597 (m) cm^{-1}. ^1H NMR (CCl_4): δ (ppm) 7.3 (m).

Dialkyl ditellurides by reduction of divinyl ditellurides with sodium borohydride in ethanol

$NaBH_4$ (0.09 g, 2.5 mmol) was added to a solution of a divinyl ditelluride (1.0 mmol) in ethanol (8 ml) (room temperature, nitrogen 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% aqueous sodium hydroxide solution (0.5 ml) were added. The resulting red solution was diluted with diethyl ether, washed with brine, dried over magnesium sulfate, filtered and the filtrate evaporated. The residue was the dialkyl ditelluride (pure by ^{1}H NMR). The dipropyl ditelluride was purified by distillation in a Kugelrohrofen at 84°C/0.45 mmHg. Yields and proton NMR data are listed in Table 1.

Isopropyl, 2-phenylethenyl telluride

$NaBH_4$ (0.09 g, 2.5 mmol) was added to a solution of dipropen-2-yl ditelluride (0.337 g, 1.0 mmol) and phenylacetylene (0.215 g, 2.1 mmol) in ethanol (8 ml) (room temperature, nitrogen atmosphere). The reaction mixture was stirred under reflux for 3 h and then treated as described above to give isopropyl-2-phenylethenyl telluride. Yield: 0.47 g, 86%. ^{1}H NMR (CCl_4/TMS): 1.65 (d, J 7 Hz, 6H); 3.28 (hept., J 7 Hz, 1H); 6.91 (d, J 11 Hz, 1H); 7.21 (s, 5H); 7.38 (d, J 7 Hz, 1H).

Alkyl vinyl tellurides from divinyl ditellurides

A solution of a divinyl ditelluride (1.0 mmol) in THF (6 ml) was added dropwise at room temperature to a nitrogen purged, round-bottomed flask containing $LiAlH_4$ (0.09 g, 2.5 mmol) in THF (3 ml). The dark red color of the ditelluride disappeared. The resulting reaction mixture was treated with butyl bromide (0.3 g, 2.2 mmol) and stirred for 15 min. Then water (0.5 ml), 10% sodium hydroxide solution (0.5 ml) and water (0.5 ml) were added in sequence. The product was extracted with diethyl ether (3 × 10 ml). The extract was washed with brine, dried over magnesium sulfate, filtered and the filtrate evaporated to give the alkyl vinyl telluride as a yellow oil (pure by ^{1}H NMR).

$CH_2{=}C(CH_3)TeC_4H_9$. Yield: 0.384 g (85%). IR(film): ν 1586 (m) cm^{-1}. ^{1}H NMR (CCl_4): δ (ppm) 0.93 (t, J 7 Hz, 3H); 1.1–2.1 (m, 4H); 2.25 (dd, J ~ 1.5 Hz, J ~ 1.0 Hz, 3H); 2.80 (t, J 7 Hz, 2H); 5.38 (q, J ~ 1 Hz, 1H); 5.85 (q, J ~ 1.5 Hz, 1H).

$CH_3CH{=}CHTeC_4H_9$. Yield: 0.37 g (82%). IR (film): ν 1585 (m) cm^{-1}. ^{1}H NMR (CCl_4): δ (ppm) 0.91 (t, J 7 Hz, 3H); 1.1–2.1 (m, 7H); 2.68 (t, J 7 Hz, 2H); 5.9–6.7 (m, 2H).

Reduction of the carbon–carbon bond in dipropen-2-yl ditelluride

A solution of dipropen-2-yl ditelluride (0.337 g, 1.0 mmol) in THF (6 ml) was added dropwise at room temperature under nitrogen to a round-bottomed flask containing $LiAlH_4$ (0.09 g, 2.5 mmol) in THF (3 ml). The dark-red color disappeared instantaneously. After 10 min of stirring at room temperature the reaction mixture was cautiously treated with water (0.5 ml) under nitrogen, the flask opened and the mixture stirred for additional 15 min at room temperature. Then 10% sodium hydroxide solution (0.5 ml) and water (0.5 ml) were added. The mixture was diluted with diethyl ether (20 ml), washed with brine, dried over magnesium sulfate, filtered and the filtrate evaporated to give a mixture of diisopropyl ditelluride and dipropen-2-yl ditelluride in a 7.7/2.3 ratio (calculated by ^1H NMR). Yield: 0.31 g.

Butyl vinyl telluride from divinyl ditelluride by reduction with lithium in liquid ammonia followed by alkylation

To a nitrogen-purged round-bottomed flask containing lithium (0.015 g, 2.2 mmol) dissolved in liquid ammonia (~ 10 ml) at −78 °C, a solution of divinyl ditelluride (0.309 g, 1.0 mmol) in THF (10 ml) was added. The color of the solution turned from blue to red. The reaction mixture was stirred for 10 min, then treated with butyl bromide (0.3 g, 2.2 mmol), and allowed to reach room temperature. After the total evaporation of ammonia, the reaction mixture was diluted with diethyl ether (20 ml) and washed with brine. The organic phase was dried over magnesium sulfate, filtered, and the filtrate evaporated. The residue was distilled in a Kugelrohrofen to give butyl vinyl telluride (pure by ^1H NMR). Yield: 0.27 g, 63%. ^1H NMR (CCL_4/TMS): 0.93 (t, J 7 Hz, 3H); 1.1–2.1 (m, 4H); 2.75 (t, J 7 Hz, 2H); 5.79 (d, J 17 Hz, 1H); 6.21 (d, J 10 Hz, 1H); 7.16 (dd, J 17, 10 Hz, 1H).

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