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The assessment of some Sb–Te single-source compounds for MOCVD applications

Ron S. Dickson *, Kerryn D. Heazle

Monash University, Department of Chemistry, Clayton, 3168 Victoria, Australia

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Abstract

The new compounds $Et_2SbTeEt$, $Me_2SbTeEt$, Et_2SbTe^iPr and $Et_2AsTeEt$ have been prepared by reactions of Et_4Sb_2, Me_4Sb_2 or Et_4As_2 with ${}^iPr_2Te_2$ or Et_2Te_2. An alternative route to $Et_2SbTeEt$ involved the reaction of Et_2SbBr with EtTeLi. The compounds are light sensitive, and some of them cannot be obtained pure because of facile radical decomposition or reverse dissociation to the corresponding R_4E_2 and R'_2Te_2. Thermal degradation of $Et_2SbTeEt$ in a hydrogen stream under conventional MOCVD condition gives a metal deposit containing Sb and Te in the ratio 1.6:1. The related compound $Et_2SbTeSbEt_2$ reacts with H_2 at room temperature to give Te metal and presumably $HSbEt_2$.

Keywords: Antimony; Arsenic; Tellurium; MOCVD

1. Introduction

Attention was recently drawn to a number of potential and actual opto-electronic applications of antimony telluride (Sb_2Te_3) and related materials such as Bi_2Te_3 and Sb_2Se_3 [1]. Reports of the formation of Sb_2Te_3 thin films seem to be limited to some sputtering and reactive evaporation approaches [2], and a very recent account [1] of room temperature MOCVD based on the reaction shown in Eq. 1. The films were grown at reduced pressure (ca. 0.25 Torr) under Sb-rich conditions. The development of single source compounds for use in the production of thin films of Sb_2Te_3 by MOCVD would be worthwhile. Antimony–tellurium single source compounds would also be a useful source of the dopant element antimony in the production of p-type 12–16 semiconductors including CdTe(Sb) and $Hg_{1-x}Cd_xTe$(Sb) [3].

$$2Sb(NMe_2)_3 + 3(Me_3Si)_2Te \longrightarrow Sb_2Te_3 + 6Me_3SiNMe_2 \qquad (1)$$

A number of organometallic compounds incorporating direct Sb–Te links are known [4]. We decided to assess the value of some compounds of the types R_2SbTeR' and $R_2SbTeSbR_2$ for possible MOCVD applications, and we report the results below.

2. Results

2.1. The preparation of R_2SbTeR' compounds

Breunig and coworkers showed [5,6] that complete dismutation occurs when distibanes and ditellurides are mixed (Eq. (2)).

$$R_2SbSbR_2 + R'TeTeR' \longrightarrow 2R_2SbTeR' \qquad (2)$$

Several products are formed ($R = CH_3$, C_2H_5; $R' = CH_3$, $p\text{-}CH_3C_6H_4$) and all are described as fairly stable. They could be distilled at reduced pressure.

Given the perceived advantage of using ethylmetal compounds for MOCVD applications, we were initially interested in the compound $Et_2SbTeEt$, which has not been described previously. We found that this compound was formed in near quantitative yield when Et_4Sb_2 is added to Et_2Te_2 at 0°C; the crude product contained small amounts of Et_3Sb, Et_2Te_2, and Et_2Te, but a spectroscopically pure product was obtained by fractional distillation, under reduced pressure.

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* Corresponding author.

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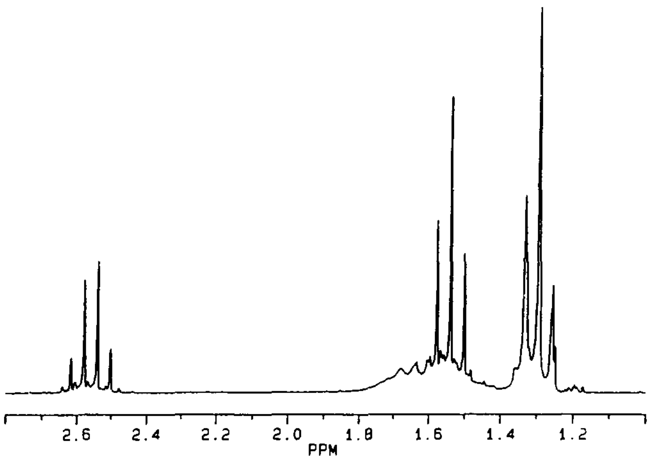


Fig. 1. ^1H NMR spectrum of $Et_2SbTeEt$.

We have also developed an alternative synthesis of $Et_2SbTeEt$ based on the reaction between bromodiethylstibane and lithium ethyltelluride (Eq. (3)). The crude product obtained from this reaction was contaminated with small amounts of Et_3Sb, Et_2Te_2 and $Et_2SbTeSbEt_2$.

$$Et_2SbBr + EtTeLi \longrightarrow Et_2SbTeEt + LiBr \qquad (3)$$

Ethyltellurodiethylstibane, $Et_2SbTeEt$, is an orange-red liquid. It is air and light sensitive, and must be stored under nitrogen in the dark to avoid decomposition. The mass spectrum shows the parent ion for $Et_2SbTeEt$ at m/z 308 with the expected Sb–Te isotope pattern. The most abundant peak appears at m/z 251, and is attributed to the fragment $SbTe^+$. This indicates that the Sb–Te bonds are relatively strong in this complex.

In the ^1H NMR spectrum of $Et_2SbTeEt$, multiplets are observed in three regions. A typical A_2B_3 pattern is observed for the ethyl group attached to Te, but the signals for the $SbEt_2$ group appear as a triplet and a broad multiplet which lies below the TeEt triplet. The spectrum is shown in Fig. 1. The broadness of the methylene–antimony signal is not readily explained, particularly because this phenomenon is not observed for the analogous compound $Et_2SbTeMe$ that is described below. The ^{13}C NMR spectrum shows resonances for two methyl and two methylene carbons as expected. Again, the signal for the CH_2–Sb group is uncharacteristically broad, with the width at half height being 10 Hz (cf. CH_2–Te, < 2 Hz). A singlet is observed in the ^{125}Te NMR spectrum at $\delta - 116$ relative to Me_2Te.

To examine further the light sensitivity of this compound, a deuterated benzene solution of $Et_2SbTeEt$ contained in an NMR tube was exposed to the light for four days. It was then possible to identify four products and unchanged starting compound from characteristic signals in the NMR spectrum. The amounts of these products as percentages of the total were: $Et_2SbTeEt$ (45), Et_3Sb (25), $Et_2SbTeSbEt_2$ (15), Et_2Te_2 (10), and Et_2Te (5). After further exposure to the light, an NMR spectrum could not be recorded because of the formation of a metal film on the walls of the NMR tube.

The same four products were formed when $Et_2SbTeEt$ was heated at 100°C in the dark. After 42 h, the thermal decomposition products (expressed as percentages of the total) were: $Et_2SbTeEt$ (11), Et_3Sb (45), $Et_2SbTeSbEt_2$ (14), Et_2Te_2 (3), and Et_2Te (27). The amounts of the two major products, Et_3Sb and Et_2Te, gradually increased over this time, whereas there was little change in the amount of $Et_2SbTeSbEt_2$ after the first 4 h and some decrease in the amount of Et_2Te_2. Again a metal precipitate was formed; this first became evident after about 11 h.

The formation of all of the above products can be accounted for in terms of a free radical mechanism. Examples of the types of reactions that may occur are shown in eqns. (4)–(8).

$$Et_2SbTeEt \longrightarrow Et_2Sb^{\cdot} + EtTe^{\cdot} \qquad (4)$$

$$Et_2SbTeEt + Et_2Sb^{\cdot} \longrightarrow Et_2SbTe^{\cdot} + Et_3Sb \qquad (5)$$

$$Et_2SbTe^{\cdot} + Et_2Sb^{\cdot} \longrightarrow Et_2SbTeSbEt_2 \qquad (6)$$

$$EtTe^{\cdot} + EtTe^{\cdot} \longrightarrow Et_2Te_2 \qquad (7)$$

$$Et_2Te_2 \longrightarrow Et_2Te + Te \qquad (8)$$

It is reported [4] that the compounds R_2SbER' (E = Se, Te) rearrange thermally to R_3Sb and $RSb(ER')_2$. However, we find no evidence from the ^{13}C NMR spectrum that $EtSb(TeEt)_2$ is formed in any of our degradation studies.

Only a minor amount of decomposition occurs when $Et_2SbTeEt$ is stored in the dark at room temperature. After three months, the total amount of impurities (Et_3Sb, Et_2Te_2, Et_2Te, and $Et_2SbTeSbEt_2$) was less than 5%.

Another new compound, $Me_2SbTeEt$, was obtained as an orange liquid by adding the distibane Me_4Sb_2 to an equimolar amount of the ditelluride Et_2Te_2. The NMR spectra showed that the crude product was contaminated with small amounts of Me_2EtSb, Me_3Sb and Et_2Te_2. Distillation at 25–30°C under dynamic vacuum removed the more volatile trialkylstibane impurities, but it was more difficult to free the product from the last traces of Et_2Te_2. The compound was characterized by multinuclear NMR and mass spectroscopy (see Experimental details).

After a deuterated benzene solution of $Me_2SbTeEt$ had been exposed to the light for two weeks, the following compounds were detected in the mixture by NMR spectroscopy: $Me_2SbTeEt$ (55), Me_2EtSb (28), Et_2Te_2 (14), Et_2Te (2) and Me_3Sb (1%). The same species were also formed when $\mathrm{Me_2SbTeEt}$ was heated in the dark.

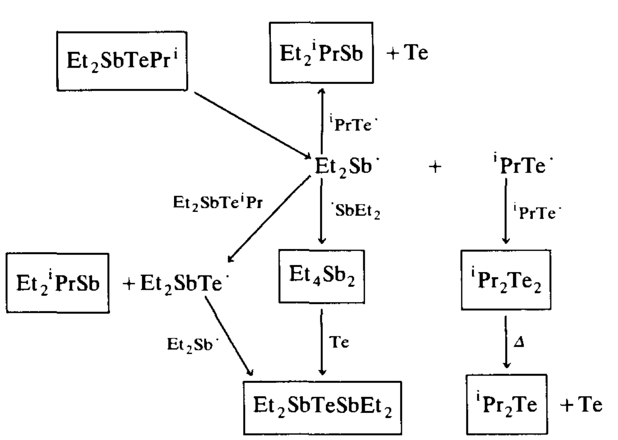
Although the related compound $\mathrm{Et_2SbTeMe}$ was already known, we decided to prepare it so that its relative stability could be determined. The reported preparation of this compound [6] involves the dismutation reaction between $\mathrm{Et_4Sb_2}$ and $\mathrm{Me_2Te_2}$. We developed a new synthesis based on the reaction between $\mathrm{Et_2SbBr}$ and MeTeLi. The crude product was obtained in high yield, but was contaminated by a small amount of $\mathrm{Et_2SbTeSbEt_2}$. Fractional distillation under vacuum separated the more volatile $\mathrm{Et_2SbTeMe}$ from a residue that contained the impurity, but the distillate was now contaminated with a small amount of $\mathrm{Me_2Te_2}$. The compound $\mathrm{Et_2SbTeMe}$ was characterized by multinuclear NMR and mass spectroscopy.

In keeping with the behaviour of the other $\mathrm{R_2SbTeR'}$ compounds, $\mathrm{Et_2SbTeMe}$ is light sensitive. After a deuterated benzene solution of the compound had been left on the laboratory bench for two days, a metallic film was evident. The ^{1}H NMR spectrum of the remaining liquid was very complex, but the ^{13}C spectrum gave a better indication of the products present. The species identified were unchanged $\mathrm{Et_2SbTeMe}$ plus $\mathrm{Et_3Sb}$, $\mathrm{Et_2Te}$, $\mathrm{Me_2Te}$ and $\mathrm{Me_2Te_2}$. Resonances for the compound $\mathrm{Et_2SbTeSbEt_2}$ were not observed. There were additional $\mathrm{CH_3}$ and $\mathrm{CH_2}$ peaks in the spectrum, but it was not possible to assign them to any other likely decomposition products.

A sample of $\mathrm{Et_2SbTeMe}$ was kept in the dark at 5°C for four months, after which the NMR spectrum had not changed. Thus $\mathrm{Et_2SbTeMe}$ is more stable than $\mathrm{Et_2SbTeEt}$ or $\mathrm{Me_2SbTeEt}$.

The possibility that the alkyl group on Te has an influence on the stability of $\mathrm{R_2SbTeR'}$ compounds was further explored by attempting to prepare $\mathrm{Et_2SbTe^iPr}$. The reaction between equimolar amounts of $\mathrm{Et_4Sb_2}$ and $\mathrm{Pr^i_2Te_2}$ gave $\mathrm{Et_2SbTe^iPr}$, but the product contained a number of impurities. The initial impurity level was lower if the reaction was performed at −60°C. However, there was evidence of a fairly rapid build-up of impurities when the crude product was kept at 5°C or above, even in the dark. Attempted purification by vacuum distillation was unsuccessful.

Multinuclear NMR analysis of the crude reaction product revealed the expected resonances for $\mathrm{Et_2SbTe^iPr}$ (see Experimental details), and established that this was the major product. The ^{13}C and ^{125}Te results showed that $\mathrm{Et_2SbTeSbEt_2}$ and $\mathrm{^iPr_2Te_2}$ were also present, and there was a much smaller amount of $\mathrm{^iPr_2Te}$. A further tellurium-free impurity was also present, and the NMR data are consistent with this being the mixed alkyl stibane $\mathrm{Et_2Sb^iPr}$. Formation of the various by-products is again accounted for in terms of radical and other reactions of the types shown in Scheme 1.



Scheme 1. Radical decomposition pathway for the compound $\mathrm{Et_2SbTe^iPr}$

To add a further dimension to our comparison of these compounds, we attempted to prepare $\mathrm{Et_2AsTeEt}$. Two $\mathrm{R_2AsTeR'}$ compounds, those with (R = Me or $\mathrm{CF_3}$ and R′ = Me), had been reported previously [7], and these were prepared from $\mathrm{Me_2Te_2}$ and the appropriate diarsane $\mathrm{R_4As_2}$.

The reaction between equimolar amounts of $\mathrm{Et_2Te_2}$ and $\mathrm{Et_4As_2}$ gave $\mathrm{Et_2AsTeEt}$, but the product was contaminated with small amounts of $\mathrm{Et_3As}$ and $\mathrm{Et_2Te_2}$. The more volatile $\mathrm{Et_3As}$ was removed by vacuum distillation, but during this process the amount of $\mathrm{Et_2Te_2}$ increased. The $\mathrm{Et_2AsTeEt}$ and $\mathrm{Et_2Te_2}$ could not be separated by fractional distillation under vacuum. In an attempt to circumvent this problem, the reaction was repeated with an excess of the diarsane. The product of this reaction contained $\mathrm{Et_2AsTeEt}$ and both free $\mathrm{Et_4As_2}$ and free $\mathrm{Et_2Te_2}$. These observations indicate that the formation of $\mathrm{Et_2AsTeEt}$ involves the equilibrium shown in eqn. (9).

$$\mathrm{Et_4As_2 + Et_2Te_2 \rightleftharpoons 2Et_2AsTeEt} \qquad (9)$$

There are precedents for this, and the formation constants for $\mathrm{Me_2PTeMe}$ and $\mathrm{Me_2AsTeMe}$ were reported [8] to be 3×10^{-2} and 63, respectively. It is evident that it will not be possible to obtain compounds of the type $\mathrm{R_2AsTeR'}$ of sufficient purity for MOCVD applications. Clearly, the compounds $\mathrm{R_2PTeR'}$ cannot be considered either.

2.2. *Attempted purification of $\mathrm{Et_2SbTeEt}$ by formation of an adduct*

The difficulty experienced in obtaining pure samples of the compounds $\mathrm{R_2SbTeR'}$ prompted us to attempt the purification of $\mathrm{Et_2SbTeEt}$ by formation of an adduct. As indicated in Fig. 2, there are lone pair electrons on both Sb and Te, so that interaction with a Lewis acid was appropriate. We chose $\mathrm{CdI_2}$ because it has been used previously to form adducts of both

Et_4Sb_2 [9] and Et_2Te [10]. When $Et_2SbTeEt$ and CdI_2 were mixed, a slow reaction occurred during several days to give Et_2SbI and an unidentified solid containing EtTe, TeI, and CdI fragments. Because these observations indicated that a cleavage reaction had occurred, this approach to the purification of R_2SbTeR' compounds was abandoned.

2.3. Assessment of $Et_2SbTeEt$ for MOCVD applications

The products formed when $Et_2SbTeEt$ is heated in a sealed tube are consistent with the initial formation of the radicals $Et_2Sb^{\cdot}$ and $EtTe^{\cdot}$. There was also evidence of formation of a metal deposit in these thermal degradation reactions. Although the mass spectrum of $Et_2SbTeEt$ also revealed independent ethylantimony and ethyltellurium fragments, some of the most intense peaks correspond to species with the intact Sb–Te unit. We decided to investigate the chemical vapour deposition of metals from $Et_2SbTeEt$ in a hydrogen stream using a horizontal reactor.

Prior to conducting the MOCVD experiments, the vapour pressure of $Et_2SbTeEt$ was determined using the Knudsen effusion method. A plot of log P against the reciprocal of the temperature was linear and corresponded to log $P = -6219\ T + 17.6$. The vapour pressure was 0.033 mm Hg at 25°C and rose to 0.791 mm at 80°C. We note that the compound is significantly more volatile than Et_4Sb_2 (0.011 mm at 25°C), which has been used successfully [9] as a precursor for antimony deposition at both dopant (CdTe:Sb) and semiconductor (InSb) levels.

In the thermal degradation experiment, pre-etched GaAs substrates were used, the temperature zone in the oven ranged from 200–400°C, and the flow rate of H_2 was 50 $cm^3\ min^{-1}$. During a 5 h period, a large amount of metal deposition was observed in the 200–250°C heat zone. The XPS spectrum for a substrate taken from this zone is shown in Fig. 3. There are no visible Ga or As peaks which indicates that at least 100 Å of material has been deposited on the substrate. Both Sb and Te peaks are evident, and the ratio of Sb to Te is about 1.6 : 1 based on comparison of peak integration for the Sb and Te $3d_{3/2}$ and 4d peaks. The amount of C in the deposit is minimal.

The reasons for deposition of an antimony-rich film have not been determined, but we note that only Sb was deposited when the CVD experiment was repeated with GaAs substrates that had not been etched. Further work would be needed to establish the gas phase decomposition pathway. Steps involving the initial formation of $Et_2Sb^{\cdot}$ and $EtTe^{\cdot}$, which subsequently react with H_2 to form the unstable species Et_2SbH and HTeEt, seem likely, but the reaction of H_2 with binuclear species such as $Et_2SbTe^{\cdot}$ may also be important.

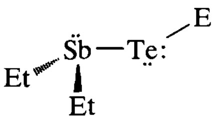


Fig. 2. The Lewis base sites in $Et_2SbTeEt$.

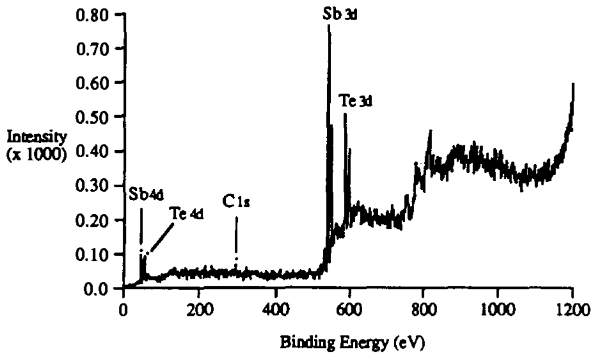


Fig. 3. The XPS of the deposit on a GaAs substrate from the CVD (H_2 atmosphere) of $Et_2SbTeEt$. The unlabelled peaks arise from Sb and Te auger electrons.

2.4. Assessment of $Et_2SbTeSbEt_2$ as an MOCVD precursor

In an earlier paper [9], we reported that Et_4Sb_2 reacts directly with Te to form $Et_2SbTeSbEt_2$ in high yield. This compound is also a by-product in some of the reactions described above. In deciding to examine this compound for possible MOCVD applications, we were encouraged by the observation that exposure of the compound to the air produces a metallic film that was found to contain a large amount of Sb_2Te_3 when analyzed by X-ray diffraction. The only other product identified was the oxide Sb_2O_3.

It is not surprising that $Et_2SbTeSbEt_2$ is less volatile than either Et_4Sb_2 or $Et_2SbTeEt$. The vapour pressure at 40°C was 0.0011 mm Hg, and extrapolation of measurements taken over the temperature range 40–80°C indicates that the vapour pressure at 20°C would be about 1.3×10^{-4} mm Hg. These vapour pressures are rather low for use of the compound in conventional MOCVD. Moreover, there was evidence of decomposition as soon as the compound was exposed to a H_2 stream. In a system set up for conventional MOCVD, separate metal deposits were evident in both the cold and hot zones of the reactor tube. Analysis of these metal deposits by XPS showed that the metal in the cold regions of the tube was mainly Te, and that the hot zone deposit contained only Sb. These results are consistent with initial hydrogenolysis of the precursor to form unstable H_2Te and Et_2SbH. It is obvious that $Et_2SbTeSbEt_2$ is not a suitable precursor for conventional MOCVD applications.

3. Experimental details

3.1. General procedures

All reactions were carried out under dry oxygen-free nitrogen or argon, using standard Schlenk techniques. Solvents were purified by standard procedures and distilled from sodium and benzophenone prior to use [11].

Tetraethyldistibane, Et_4Sb_2, and tetramethyldistibane, Me_4Sb_2, were prepared as described previously [9]. The same procedure was used to prepare tetraethyldiarsane, Et_4As_2. Two methods were used to prepare the dialkylditellurides, R_2Te_2 (R = Et, ^{i}Pr). One is an adaptation of a published procedure [12] and involved treatment of the alkali metal telluride M_2Te_2 ($M = NaK_{2.8}$), suspended in tetrahydrofuran, with the appropriate alkyl halide. The other involved treatment of Te powder in tetrahydrofuran with superhydride and subsequently with the alkyl halide [13]. In each case, solvent was removed under vacuum, and the red residue was extracted with pentane. Subsequent removal of pentane from the extract gave a deep red liquid with a pungent odour. Fractional distillation under vacuum separated the R_2Te_2 compound from any R_2Te.

Bromodiethylstibane, Et_2SbBr, was prepared by the thermal decomposition of Et_3SbBr_2 as described previously [14]. GaAs(100) substrates were purchased from American Xtal Technology, Dublin, California, USA. Before use, they were degreased in acetone, rinsed in water and then etched in a mixture of $H_2SO_4 : H_2O_2 : H_2O$, (5 : 1 : 1 by volume). After a further washing with water, the substrates were dried in a stream of N_2 and used immediately.

NMR spectra were recorded on Bruker AC-200 or AM-300 spectrometers. All NMR spectra were recorded in deuterated benzene; the C_6H_6 peak (δ 7.15 for ^{1}H and δ 128.0 for ^{13}C) was used as internal reference. ^{125}Te chemical shifts are reported upfield from the external reference Me_2Te. Mass spectra were recorded on a VG TR10-1 GC-MS instrument. UV-Vis spectra were recorded using a Cary 3 spectrophotometer. Vapour pressures were calculated from mass loss recorded on a Cahn R100 series Microbalance using the Knudsen effusion method [15]. The XPS data were obtained using a vacuum generators (VG) HB-100 electron spectrometer, which operates at a base pressure of better than 10^{-10} mbar. A VG AG-60 ion gun was used to produce argon ions which were employed to clean away surface contaminants. X-rays were generated by a dual-anode (Mg/Al) source, utilizing the Al Kα line (1486.6 eV), which was operated at 15 kV and 32 mA. The resulting photoelectrons were analysed with a VG CLAM-100 150° spherical sector electrostatic analyzer, which was operated in the constant analyser energy (CAE) mode with a pass energy of 50 eV. The data collection and processing were performed by a DEC 11/23 minicomputer. Powder X-ray diffraction patterns were recorded on a Scintag PAD V powder diffractometer with a Ge solid-state detector.

3.2. Preparation of ethyltellurodiethylstibane, $Et_2SbTeEt$

Two methods were used to prepare $Et_2SbTeEt$, and these are outlined below.

3.2.1. Reaction of Et_4Sb_2 with Et_2Te_2

This procedure was based on that used by Breunig and Gülec [5]. In a typical reaction, Et_4Sb_2 was added dropwise to one equivalent of Et_2Te_2 at 0°C until the deep-red colour of the ditelluride disappeared. The orange-red liquid product $Et_2SbTeEt$ was obtained in near quantitative yield.

The NMR spectra indicated that the $Et_2SbTeEt$ was always contaminated with small amounts of three impurities (total less than 5%). These were identified as Et_3Sb (^{1}H; δ 1.19 (m, $\mathrm{SbC}H_2\mathrm{C}H_3$): ^{13}C; δ 5.88 ($\mathrm{Sb}C\mathrm{H}_2$), 11.82 ($\mathrm{Sb}C\mathrm{H}_3$)}, Et_2Te_2 {^{1}H; δ 1.40 (t, ^3J (H–H) = 8 Hz, $\mathrm{TeC}H_3$), 2.67 (q, ^3J (H–H) = 8 Hz, $\mathrm{TeC}H_2$): ^{13}C; δ −4.99 ($\mathrm{Te}C\mathrm{H}_2$), 19.80 ($\mathrm{Te}C\mathrm{H}_3$)}, and Et_2Te {^{1}H; δ 1.40 (t, ^3J (H–H) = 8 Hz, $\mathrm{TeC}H_3$), 2.33 (q, ^3J (H–H) = 8 Hz, $\mathrm{TeC}H_2$): ^{13}C; δ −5.96 ($\mathrm{Te}C\mathrm{H}_2$), 17.71 ($\mathrm{Te}C\mathrm{H}_3$)}.

Most of the Et_3Sb and Et_2Te was removed by pumping on the compound under vacuum; this did not remove the less volatile species Et_2Te_2. Repeated fractional distillation of the contaminated material at 80°C under a dynamic vacuum gave a spectroscopically pure product. Spectroscopic data: ^{1}H NMR spectrum (C_6D_6); δ 1.29 (psuedo-triplet, 6H, $\mathrm{SbCH_2C}H_3$), 1.40–1.80 (br.s, 4H, $\mathrm{SbC}H_2\mathrm{CH_3}$), 1.53 (t, ^3J (H–H) = 8 Hz, 3H, $\mathrm{TeCH_2C}H_3$), 2.55 (q, ^3J (H–H) = 8 Hz, 2H, $\mathrm{TeC}H_2\mathrm{CH_3}$). ^{13}C NMR spectrum ($C_6D_6$); δ −10.66 (s, $\mathrm{Te}C\mathrm{H_2CH_3}$), 5.69 (br.s, $\mathrm{Sb}C\mathrm{H_2CH_3}$), 13.71 (s, $\mathrm{SbCH_2}C\mathrm{H_3}$), 21.24 (s, $\mathrm{TeCH_2}C\mathrm{H_3}$). ^{125}Te NMR spectrum (C_6H_6 (95%) to C_6D_6 (5%) by vol.); δ −116.0 (s). Mass spectrum: m/z (relative intensity, assignment): 338 (62%, M), 309 (71%, M–Et), 281 (92%, $[SbTeEtH]^+$), 251 (100%, $[SbTe]^+$), 208 (7%, $[SbEt_3]^+$), 179 (6%, $[SbEt_2]^+$), 153 (15%), 151 (33%), 149 (20%) [the peaks at m/z 153–149 result from overlap of $[SbEtH]^+$ (151) and $[SbC_2H_4]^+$ (149)}, 150 (13%, $[SbEt]^+$), 130 (8%, $[Te]^+$), 121 (19%, $[Sb]^+$). UV-Vis spectrum (pentane), λ_{max} nm (ε mol dm^{-3}): 220 (2.04×10^4), 281 (5.26×10^3). Vapour pressure, mm Hg (temp.,°C): 0.019 (18); 0.033 (25); 0.123 (40); 0.220 (50); 0.380 (60); 0.520 (70); 0.791 (80).

Exposure of a sample of $Et_2SbTeEt$ to normal laboratory light showed that it is light sensitive. After 2 d exposure, some metal precipitate was observed and the colour of the liquid had changed from orange-red to deep red. A solution of $Et_2SbTeEt$ in C_6D_6 in an NMR tube was exposed to the light for 4 d. After this time, five products were detected from the NMR spectrum. They were identified from characteristic chemical shifts (see above) as $Et_2SbTeEt$, Et_3Sb, $Et_2SbTeSbEt_2$ {^{1}H; δ 1.31 (pseudo-triplet, $\mathrm{SbC}H_3$), 1.58 (m, $\mathrm{SbC}H_2$), 1.77 (m, $\mathrm{SbC}H_2$): ^{13}C; δ 7.71 ($\mathrm{Sb}C\mathrm{H}_2$), 13.60 ($\mathrm{Sb}C\mathrm{H}_3$)}, Et_2Te_2 and Et_2Te in an approximate ratio of 45:25:15:10:5. An NMR spectrum could not be recorded after further exposure to the light because of the formation of a metal film on the walls of the NMR tube.

3.2.2. Reaction of EtTeLi with Et_2SbBr

Ethyllithium was prepared in ether from EtI and Li by the standard method [16]. The solution was added to a frozen suspension of Te powder in THF [17]. The mixture was allowed to warm to room temperature and then was stirred until the Te was consumed and the solution was pale yellow-green. This solution was then used immediately.

The bromide Et_2SbBr (1.40 g, 5.39 mmol) was added dropwise to one equivalent of the EtLiTe solution (based on Te) and the solution immediately became a bright-orange colour. When all the Et_2SbBr had been added, the solution turned yellow. The solution was stirred at ambient temperature for 2 h. Solvent was removed under vacuum to give a white precipitate and an orange oil. The residue was extracted with pentane (3 × 20 ml) and the extracts were transferred to a new Schlenk flask through a cannula. The white solid (LiBr) remaining in the initial flask was discarded. Subsequent removal of pentane under vacuum gave an orange-red liquid (1.55 g, 85%). The crude product was analysed by NMR spectroscopy. The major component was $Et_2SbTeEt$, but small amounts of $Et_2SbTeSbEt_2$, Et_2Te_2 and Et_3Sb were also detected. The approximate ratio of these compounds was 87:8:3:2.

3.3. Preparation of ethyltellurodimethylstibane, $Me_2SbTeEt$

One equivalent of Me_4Sb_2 (0.73 g, 2.40 mmol) was added dropwise to Et_2Te_2 (0.75 g, 2.39 mmol) at 0°C to give a red liquid (1.44 g). The mixture was left for 1 d. After this time, a black metallic precipitate was observed in the flask. The liquid was filtered, and the ^{1}H NMR spectrum of the filtrate was recorded. The product was found to be contaminated with small amounts (less than 5%) of three impurities. These were identified from characteristic peaks in the ^{1}H NMR spectrum as Me_3Sb {δ 0.60 (s, $\mathrm{SbC}H_3$)}, Me_2EtSb {δ 0.58 (s, $\mathrm{SbC}H_3$, 6H), 1.17 (m, $\mathrm{SbCH_2C}H_3$, 5H)}, and Et_2Te_2 {δ 1.40 (t, ^3J H-H = 8 Hz, 3H, $\mathrm{TeCH_2C}H_3$), 2.67 (q, ^3J H-H = 8 Hz, 2H, $\mathrm{TeCH_2CH_3}$)}.

Distillation of the mixture at 25-30°C (bath temperature) under a dynamic vacuum resulted in removal of the alkylantimony compounds, but the product was still contaminated with Et_2Te_2 (ca. 4%). The $Me_2SbTeEt$ was characterized spectroscopically. ^{1}H NMR spectrum (C_6D_6): δ 1.13 (s, 6H, $\mathrm{SbC}H_3$), 1.52 (t, ^3J (H-H) = 8 Hz, 3H, $\mathrm{TeCH_2C}H_3$), 2.54 (q, ^3J (H-H) = 8 Hz, 2H, $\mathrm{TeCH_2CH_3}$). ^{13}C NMR spectrum (C_6D_6): δ −9.89 (s, $\mathrm{Te}C\mathrm{H_2CH_3}$), −5.15 (s, $\mathrm{Sb}C\mathrm{H_3}$), 21.04 (s, $\mathrm{TeCH_2}C\mathrm{H_3}$). ^{125}Te NMR spectrum (C_6H_6 (95%) to C_6D_6 (5%) by vol.): δ −20.9 (s). Mass spectrum: m/z (relative intensity, assignment) 310 (64%, M), 295 (52%, M-Me), 281 (100%, $[\mathrm{SbTeEtH}]^+$), 280 (22%, $[\mathrm{SbTeEt}]^+$), 267 (81%, $[\mathrm{SbTeMeH}]^+$), 251 (60%, $[\mathrm{SbTe}]^+$), 179 (3%, $[\mathrm{SbEt_2}]^+$), 150 (5%, $[\mathrm{SbEt}]^+$), 153 (9%), 151 (30%), 149 (33%) {the peaks at m/z 153-49 result from overlap of $[\mathrm{SbEtH}]^+$ (151), $[\mathrm{SbMe_2}]^+$ (151) and $[\mathrm{SbC_2H_4}]^+$ (149)}, 136 (20%, $[\mathrm{SbMe}]^+$), 130 (7%, $[\mathrm{Te}]^+$), 121 (18%, $[\mathrm{Sb}]^+$).

After exposure of the NMR solution to the light for two weeks, the NMR spectrum was recorded again. This revealed the presence of the products $Me_2SbTeEt$, Et_2Te_2, Et_2Te, Me_2EtSb, and Me_3Sb in an approximate ratio of 55:14:2:28:1. A small amount of a metallic precipitate was observed in the NMR tube.

3.4. Preparation of methyltellurodiethylstibane, $Et_2SbTeMe$

The reagent MeTeLi was prepared in Et_2O from MeLi and Te [17]. The compound Et_2SbBr (1.20 g, 4.62 mmol) was added dropwise to one equivalent of the MeTeLi solution (based on Te) and the resulting orange solution was stirred at room temperature for 2 h. Removal of solvent under vacuum yielded a white precipitate and an orange oil. The residue was extracted with pentane (3 × 20 ml) and the pentane extracts were combined in a new Schlenk flask. Subsequent removal of pentane under vacuum gave $Et_2SbTeMe$ (1.27 g, 85%) as an orange liquid. Small amounts of $Et_2SbTeSbEt_2$ and Me_2Te_2 were detected in this product by NMR spectroscopy. Distillation of the mixture at 35-40°C under a dynamic vacuum gave $Et_2SbTeMe$ that was still contaminated with a small amount (less than 4%) of Me_2Te_2 {^{1}H: δ 2.28 (s, Te satellites 24 Hz, $\mathrm{TeC}H_3$)}. The $Et_2SbTeMe$ was characterized spectroscopically. ^{1}H NMR spectrum (C_6D_6): δ 1.27 (pseudo-triplet, 6H, $\mathrm{SbCH_2C}H_3$), 1.35-1.75 (m, 4H, $\mathrm{SbC}H_2\mathrm{CH_3}$), 1.70 (s, 3H, $\mathrm{TeC}H_3$). ^{13}C NMR spectrum (C_6D_6): δ −29.83 (s, $\mathrm{Te}C\mathrm{H_3}$), 5.88 (s, $\mathrm{Sb}C\mathrm{H_2CH_3}$), 13.70 (s, $\mathrm{SbCH_2}C\mathrm{H_3}$). ^{125}Te NMR spectrum (C_6H_6 (95%) to C_6D_6 (5%) by vol.): δ −327.9 (s). Mass spectrum: m/z (relative intensity, assignment) 324 (72%, M), 295 (73%, M-Et), 281 (14%, $[\mathrm{SbTeEtH}]^+$), 267 (100%, $[\mathrm{SbTeMeH}]^+$), 266 (22%, $[\mathrm{SbTeMe}]^+$), 251 (94%, $[\mathrm{SbTe}]^+$), 179 (6%, $[\mathrm{SbEt_2}]^+$), 150 (8%, $[SbEt]^+$), 153 (9%), 151 (25%), 149 (33%) (the peaks at m/z 153–149 result from overlap of $[SbEtH]^+$ (151) and $[SbC_2H_4]^+$ (149)), 130 (5%, $[Te]^+$), 121 (18%, $[Sb]^+$).

A sample of $Et_2SbTeMe$ in an NMR tube was exposed to the light for 2 d after which a metal film was present. The ^1H NMR spectrum was quite complicated but characteristic resonances for Et_2Te, Et_3Sb and Me_2Te_2 were discernible. Peaks observed in the ^{13}C NMR spectrum allowed the further identification of Me_2Te [18] and the starting material $Et_2SbTeMe$ in the mixture. Two additional significant peaks were observed in the ^{13}C NMR spectrum at δ 15.39 (CH_3) and δ7.22 (CH_2).

3.5. *Attempted preparation of isopropyltellurodiethylstibane, Et_2SbTe^iPr*

The compound $^iPr_2Te_2$ (0.61 g, 1.79 mmol) was added dropwise to Et_4Sb_2 (0.64 g, 1.78 mmol) at 0°C. Initially, an orange liquid was produced and then the mixture darkened and a metallic film formed on the walls of the Schlenk flask. The final liquid was dark brown with a fine black precipitate. Pentane (50 ml) was added and the mixture was filtered through Celite to give an orange filtrate. Solvent was removed from the filtrate under vacuum to give a deep red-orange liquid (1.15 g). The liquid was unstable, depositing further quantities of metal, even though it was stored in the dark at 5°C. The NMR spectra of a freshly filtered sample of the liquid were recorded in C_6D_6. The NMR resonances for the major product Et_2SbTe^iPr are listed below. ^1H NMR spectrum (C_6D_6): δ 1.21 (pseudo-triplet, 6H, $SbCH_2CH_3$), 1.40–1.90 (m, 4H, $SbCH_2CH_3$), 1.62 (d, ^3J (H–H) = 8 Hz, 3H, $TeCH(CH_3)_2$), 3.37 (sept, ^3J (H–H) = 8 Hz, 2H, $TeCH(CH_3)_2$). ^{13}C NMR spectrum (C_6D_6): δ 6.92 (s, $TeCH(CH_3)_2$), 5.21 (s, $SbCH_2CH_3$), 13.85 (s, $SbCH_2CH_3$), 31.02 (s, $TeCH(CH_3)_2$). ^{125}Te NMR spectrum (C_6H_6 (95%) to C_6D_6 (5%) by vol.): δ 70.8 (s).

The NMR spectra showed that the desired product Et_2SbTe^iPr, was contaminated with large amounts of $^iPr_2Te_2$ {^1H; δ 1.44 (t, ^3J (H–H) = 8 Hz, $TeCH(CH_3)_2$), 3.14 (sept, ^3J (H–H) = 8 Hz, $TeCH(CH_3)_2$): ^{13}C; δ 28.62 ($TeCH(CH_3)_2$) and 9.35 ($TeCH(CH_3)_2$): ^{125}Te; δ 274.8 (s)}, $^iPr_2Te$ {^1H; δ 1.49 (t, ^3J(H–H) = 8 Hz, $TeCH(CH_3)_2$), 3.16 (sept, ^3J(H–H) = 8 Hz, $TeCH(CH_3)_2$): ^{13}C; δ 27.56 ($TeCH(CH_3)_2$) and 10.21 ($TeCH(CH_3)_2$): ^{125}Te; δ 675.2 (s)} and $Et_2SbTeSbEt_2$ {^1H; δ 1.31 (pseudo-triplet, $SbCH_2CH_3$), 1.58 (m, $SbCH_2CH_3$), 1.77 (m, $SbCH_2CH_3$): ^{13}C; δ 7.71 ($SbCH_2CH_3$) and 13.60 ($SbCH_2CH_3$): ^{125}Te; δ 725.7 (s)}

Additional peaks were observed in the ^{13}C NMR spectrum at δ 21.95 (CH or CH_3), 16.77 (CH or CH_3), 12.13 (CH or CH_3), 6.06 (CH_2) in a ratio of 3:1:2:2. A multiplet was also observed in the ^1H NMR spectrum at δ 1.19.

When the reaction was repeated at temperatures as low as −60°C, the same products were obtained, although the amounts of impurities present were lower at lower temperatures.

3.6. *Attempted preparation of ethyltellurodiethylarsane, $Et_2AsTeEt$*

The compound Et_2Te_2 (0.56 g, 1.79 mmol) was added dropwise to Et_4As_2 (0.47 g, 1.77 mmol) at 0°C. A red liquid was obtained, and it was identified by NMR spectroscopy (see below) as $Et_2AsTeEt$. The yield was near quantitative, but NMR spectroscopy indicated that small amounts of Et_2Te_2 and Et_3As were present. The product was distilled at 40°C (bath temperature) under a dynamic vacuum, but the NMR spectra indicated that the distillate was a mixture of $Et_2AsTeEt$ and Et_2Te_2 in the ratio 9:1. More Et_4As_2 was added in an attempt to remove the excess of Et_2Te_2; the ^1H NMR spectrum indicated a decrease in the amount of Et_2Te_2 (ca. 5%), but two additional peaks corresponding to free Et_4As_2 were present in the ^{13}C NMR spectrum.

In a further experiment, an excess of Et_4As_2 was added to Et_2Te_2 (1.5:1). NMR spectroscopy showed the ratio of $Et_2AsTeEt$ to Et_2Te_2 to Et_4As_2 in the mixture to be 7:1:1. The $Et_2AsTeEt$ in these mixtures was identified spectroscopically. ^1H NMR spectrum (C_6D_6): δ 1.17 (pseudo-triplet, 6H, $AsCH_2CH_3$), 1.40–1.80 (m, 4H, $SbCH_2CH_3$), 1.53 (t, ^3J (H–H) = 8 Hz, 3H, $TeCH_2CH_3$), 2.55 (q, ^3J (H–H) = 8 Hz, 2H, $TeCH_2CH_3$). ^{13}C NMR spectrum (C_6D_6): δ −7.43 (s, $TeCH_2CH_3$), 12.92 (s, $SbCH_2CH_3$), 17.70 (s, $SbCH_2CH_3$), 20.00 (s, $TeCH_2CH_3$). ^{125}Te NMR spectrum (C_6H_6 (95%) to C_6D_6 (5%) by vol.): δ 131.4. Mass spectrum: m/z (relative intensity, assignment) 314 (5%, $[Et_2Te_2]^+$), 292 (68%, M), 263 (52%, M-Et), 235 (100%, $[AsTeEtH]^+$), 205 (62%, $[AsTe]^+$), 157 (9%, $[TeEt]^+$), 130 (10%, $[Te]^+$), 105 (37%, $[AsTeH]^+$), 104 (34%, $[AsEt]^+$), 75 (5%, $[As]^+$).

3.7. *Attempted adduct purification of $Et_2SbTeEt$*

A solution of CdI_2 (1.15 g, 3.14 mmol) in THF (20 ml) was added to one of $Et_2SbTeEt$ (0.53 g, 1.58 mmol) in THF (10 ml). No immediate reaction was apparent, but after 1 d, a small amount of yellow precipitate had been formed. After a further 3 d, the yellow mother liquor was decanted from the precipitate. The yellow precipitate was washed with pentane (2 × 20 ml). The mass of the remaining material was 0.21 g. m.p. < 150°C dec. Mass spectrum: (relative intensity, assignment) m/z 314 (5%, $[Te_2Et_2]^+$), 285

(5%, $[Te_2Et]^+$), 257 (7%, $[TeI]^+$), 188 (100%, $[TeEt_2]^+$), 160 ($[TeEtH]^+$), 156 (68%, $[EtI]^+$), 130 (60%, $[Te]^+$), 72 (40%, $[C_4H_8O]^+$), 71 (48%, $[C_4H_7O]^+$). Later scans also show peaks associated with CdI_2 and $TeEt_2$. Electron microprobe and EDX analysis showed the presence of Te, Cd and I, but no Sb was present.

The solvent was removed from the yellow mother liquor under vacuum to leave an orange-yellow precipitate and some red oil. The oil was extracted with pentane and was characterised by NMR spectroscopy as Et_2SbI (0.45 g). The orange-yellow precipitate (1.05 g) appears to be the same as the initial yellow precipitate (mass spectrum and microprobe). The precipitate was not studied further.

3.8. Thermal behaviour of the Sb–Te compounds

3.8.1. $Et_2SbTeEt$

A sample of $Et_2SbTeEt$ (ca. 1.5 g) contained in a nitrogen-filled Schlenk flask was heated in the dark at 100°C and samples were withdrawn via syringe at particular intervals. These samples were dissolved in C_6D_6 and the NMR spectra recorded. A metal film/precipitate was first observed in the Schlenk flask after 11 h of heating at 100°C. Once again, the five products $Et_2SbTeEt$, Et_3Sb, $Et_2SbTeSbEt_2$, Et_2Te_2 and Et_2Te were detected in the mixture. The approximate ratios of these products (expressed as a percentage of the total) at various time intervals are listed below.

3.8.2. $Me_2SbTeEt$

A sample of $Me_2SbTeEt$ was heated at 100°C for 5 h. NMR analysis of the resultant liquid showed that it contained $Me_2SbTeEt$, Et_2Te_2, Et_2Te, Me_2EtSb and Me_3Sb in a ratio of 28:9:1:10:2.

3.8.3. $Et_2SbTeSbEt_2$

The compound $Et_2SbTeSbEt_2$ was heated at 100°C for an extended period. Samples of the material were taken at appropriate intervals and dissolved in C_6D_6, and the ^1H and ^{13}C NMR spectra were recorded. After 5 h, three products, $Et_2SbTeSbEt_2$, Et_3Sb and Et_2Te, were detected in the mixture in an approximate ratio of 25:5:3. After a further 18 h, the ratio of these products was 1:2:1. A metal deposit was first observed after 5 h of heating.

3.9. MOCVD experiments

In a typical experiment, a Pyrex tube (length 55 cm, diameter 2.5 cm) was placed inside a Lindberg model 55035 horizontal tube furnace. The furnace was then set to 400°C maximum and the entire system was flushed with pre-dried and deoxgenated N_2 for at least 0.5 h. After this time, several etched GaAs substrates were placed at intervals inside the pyrolysis tube. They were positioned by use of a glass rod with the nitrogen flow maintained. The compound (ca. 0.1–0.2 g) was introduced from a syringe into a well at the mouth of the pyrolysis tube. The gas was then switched to pre-dried and deoxgenated H_2, and the flow rate adjusted to 50 $cm^3\ min^{-1}$ using a flow meter. The exhaust gases were passed through a paraffin oil bubbler and vented in a well-ventilated fume cupboard. The experiment was generally continued until a significant metal deposit was observed in the pyrolysis tube or until the organometallic source was used up. Treatment times generally ranged from 3–5 h. After this time, the tube was allowed to cool to ambient temperature and the gas was switched to N_2. The apparatus was then disconnected under a N_2 atmosphere. The substrates were removed from the tube and stored in small sample vials, which were flushed with N_2. The substrates were then analysed by XPS spectroscopy, generally within 24 h from deposition.

3.9.1. $Et_2SbTeEt$

The compound $Et_2SbTeEt$ was decomposed by heating in a stream of H_2 (50 $cm^3\ min^{-1}$) during 5 h. A metal deposit was observed in the 200–300°C region of the furnace. Analysis of a substrate from the 250–300°C region of the furnace revealed peaks associated with both Te and Sb. The ratio of Sb to Te was 1.6:1.

3.9.2. $Et_2SbTeSbEt_2$

A sample of $Et_2SbTeSbEt_2$ was loaded into the well of the pyrolysis apparatus. When the flow of H_2 gas (50 $cm^3\ min^{-1}$) was started the compound began to decompose in the sample well and dark-grey metal film was observed on the glass surrounding the well. The decomposition experiment was continued for 6 h, even after this time, no metallic film was evident in the heated zone of the apparatus. Analysis by XPS spectroscopy of a substrate taken from the 400–450°C zone

Table 1

Time (h)	$Et_2SbTeEt$ (%)	Et_3Sb (%)	$Et_2SbTeSbEt_2$ (%)	Et_2Te_2 (%)	Et_2Te (%)
1	67	11	11	11	0
11	58	13	17	9	3
42	11	45	14	3	27

of the furnace showed only peaks associated with Sb. A sample of the material scraped from the glass walls surrounding the well was analysed by X-ray diffraction, which revealed that it was mainly Te metals.

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