Evidence for a free radical mechanism in the decomposition of bis(but-2-enyl)tellurium

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Abstract

Reactions of basic aqueous solutions of Na_2Te with $MeCH=CHCH_2Br$ or $CH_2=CHCHMeCl$ give *ZZ-*, *ZE-* and *EE-*($MeCH=CHCH_2$)$_2Te$. This is interpreted in terms of a mechanism involving attack of Na_2Te on the 2-butenyl cation formed from the allyl halide under the basic reaction conditions. The rate of reaction to give the *E*-configuration is *ca.* 3 times that to form the *Z*. Decomposition of ($MeCH=CHCH_2$)$_2Te$ in the liquid or gas phases gives all possible products arising from dimerization of the allyl group. This is interpreted in terms of homolytic fission of the Te–C bond followed by coupling of the allyl radicals formed, particularly as no compounds containing $CH_2=CHCHMeTe$ are recovered after partial pyrolysis. The products can be fitted to a purely statistical model in which the reactivity ratio of the primary to secondary allyl is *ca.* 0.63 : 0.37. The statistical fit is taken to indicate that mechanisms other than that involving homolytic fission and free radical coupling play a negligible part.

1. Introduction

Tellurium alkyls have recently become of considerable interest since they are the precursors of choice for the growth of tellurium containing semi-conductors (CdTe, CdHgTe, ZnTe, *etc.*) by the technique of metal organic vapour phase epitaxy (MOVPE) [1–3]. Currently, it is highly desirable to reduce the temperature at which the growth occurs in order to reduce the problems associated with in-diffusion from the substrate or in multi-layer structures, to increase abruptness of interfaces and to reduce mercury vacancies in as-grown material.

Various different approaches to obtaining a lower growth temperature have been devised but amongst the most successful is the use of diallyltellurium [4]. Despite its sensitivity to light [5], diallyltellurium has been successfully employed for the growth of CdTe at temperatures as low as 180°C [4]. Methyl(allyl)tellurium has also been shown to be useful for low tem-

perature growth of CdTe [6] but, in this case the compound is photochemically stable [5].

Despite this considerable interest in the applications of allyl tellurium compounds, rather little is known about the mechanisms of how they operate. It has been reported that the major decomposition product of (allyl)$_2$Te is hexa-1,5-diene [7] suggesting either a reductive coupling of the two allyl groups (Scheme 1a) or homolytic fission of the Te–C bond followed by coupling of the allyl radicals formed (Scheme 1b). It is known that coupling of allyl radicals is favoured over
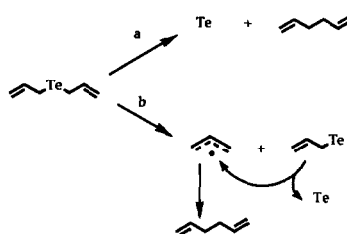
Scheme 1. Possible decomposition mechanisms for diallyltellurium: (a) reductive coupling or (b) homolytic cleavage of the Te–C bond.

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disproportionation to propene and allene by a factor of ca. 100 [8]. There has also been a brief report [9] of the decomposition, in the injection port of a gas chromatograph, of bis(3-methylbut-2-enyl)tellurium which gives a mixture of three products, each of formula $C_{10}H_{18}$. Although these were not fully identified, it was assumed that they were formed by head-to-head, head-to-tail and tail-to-tail dimerization of the 3-methylbutenyl radical formed by homolytic cleavage of the Te–C bonds, although it was not possible to rule out isomerization of the starting bis(3-methylbut-2-enyl)tellurium via a 1,3-tellura shift followed by reductive coupling of the allyl groups. The ene reaction was shown not to play a significant part in the decomposition of $(allyl)_2Te$ [9]. We have shown that radicals are formed during the liquid phase pyrolysis of various dialkyltellurium compounds [10], as well as during the gas phase pyrolysis of dipentenyl and dihexenyl tellurium [11]. In order to try to establish the mechanism of decomposition of di(allyl)tellurium compounds, it is necessary to design a compound in which the two ends of the allyl groups have different substitution patterns. Ideally, the allyl group would be $CH_2=CH-CD_2-$, but since the method that we use for synthesis of the diallyltellurium compounds probably passes through a symmetrical allyl cation, it is not possible to prevent isomerization such that compounds containing both the CH_2 and the CD_2 ends of the allyl group bound directly to the tellurium atoms are formed.

We have, therefore, investigated the preparation and decomposition of $(MeCH=CHCH_2)_2Te$.

2. Experimental details

NMR spectra were recorded on a Brüker AM300 spectrometer operating in the Fourier Transform mode with (for ^{13}C and ^{125}Te) noise proton decoupling. GC-MS studies were carried out on an INCOS 50 GC-MS with a Hewlett Packard 5890 gas chromatograph.

Quantitative GLC analyses were carried out on a Phillips PU 4500 chromatograph with a 3% OV101 column at 60°C using N_2 as the carrier gas.

1-Bromobut-2-ene (Aldrich) consisted of a mixture of E (71%) and Z (14.5%) isomers together with 3-bromobut-1-ene (14.5%). 3-Chlorobut-1-ene (Aldrich) was pure. Both were used as supplied. All manipulations were carried out in a dedicated fume-cupboard under dry oxygen-free nitrogen using standard Schlenk line and catheter tubing techniques. All vents to air were scrubbed through aqueous NaOCl.

2.1. Bis(but-2-enyl)tellurium

(a) 1-Bromobut-2-ene (56.5 cm³, 0.55 mol) was added to a solution of Na_2Te (47.5 g, 0.28 mol) in water (1 dm³) containing NaOH (100 g, 2.5 mol). The resulting two phase mixture was refluxed for 3 h, cooled to room temperature and the orange organic layer extracted with diethyl ether (3 × 100 cm³). The combined ether extracts were dried over $CaCl_2$ and the ether removed by distillation at 1 atm. After removal of all the ether, the product was distilled at 80°C in vacuo. Yield 47.6 g, 73%. On standing, a small amount of an unidentified crystalline material separated and was removed by decantation.

(b) As above but using Na_2Te (14 g, 0.08 mol), water (500 cm³), NaOH (45 g, 1.13 mol) and 3-chlorobut-1-ene (8 cm³, 0.08 mol) in ethanol (50 cm³). The reaction was carried out over 16 h at ambient temperature and the product isolated in a similar way, ethanol being removed with the diethyl ether. Yield 6.6 g, 35% (69% based on 3-chlorobut-1-ene).

2.2. Decomposition studies

2.2.1. Liquid phase

Neat $(CH_3CH=CHCH_2)_2Te$ was heated in a glass vessel connected to a condenser and collection vessel. At 165°C, a colourless liquid began to distil. This was

TABLE 1. ^1H, ^{13}C, and ^{125}Te data for bis(but-2-enyl)tellurium compounds [a]

Compound	^1H $\delta(J)$				^{13}C δ				^{125}Te δ	
	Me	CH_2	MeCH	CH_2CH	Me	CH_2	MeCH	CH_2CH	Te	Ratio
EE	1.75 (7, 0.7)	3.35 (8, 1.6)	5.4m	5.7m	17.8	5.8	125.21	130.6	14.7	56.4 (56.3) [b]
ZE E	1.75 (7, 0.7)	3.40 (7, 1.6)	5.4m	5.7m	17.8	5.5	125.24	130.6		
									28.1	37 (37.5)
Z	1.70 (8, 0.2)	3.46 (8)	5.4m	5.7m	12.7	0	124.0	129.2		
ZZ	1.70 (8, 0.2)	3.51 (8)	5.4m	5.7m	12.65	−0.2	124.1	129.1	31.7	6.5 (6.25)

[a] As neat liquids containing ca. 5% C_6D_6, 298 K; δ in ppm to high frequency of tetramethyl silane or Me_2Te, J in Hz, all couplings are doublet unless otherwise state. [b] Expected for an E/Z reactivity ratio of 3:1.

TABLE 2. ^{1}H NMR spectra of products obtained on pyrolysis of $(MeCH=CHCH_2)_2Te$

	T (°C)	MeC=	MeC=	$-CH-CH_2$	CH=CH	CH=CH$_2$	CH=CH_2
δ							
intensities		1.0	1.7	2.1	5.5	5.8	5.0
Liquid	165	23	39.5	34	25	a	15
Gas	300	23	39.1	31.3	20.7	6.9	13.8
Gas	350	23	39	32.5	27.5	8.5	16.5
Calculated [b]		23	39.2	33.8	26.1	7.7	15.3

[a] Obscured by overlap in the starting material. [b] Assuming a reactivity ratio of 0.37:0.63 for CH_2=CHCHMe˙ MeCH=CHCH$_2$˙.

collected and analysed by ^{13}C, ^{1}H and ^{125}Te NMR spectroscopy as well as by GC-MS.
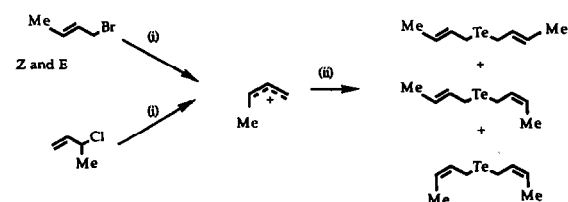
2.2.2. Gas phase

$(CH_3CH=CHCH_2)_2Te$ was distilled in vacuo through a glass tube 30 cm long and 2.5 cm in diameter heated to 300 or 350°C. The effluent from the heated tube was collected in a trap held at -196°C. A black deposit of tellurium collected in the outlet of the tube and the colourless liquid product was warmed to room temperature. It was distilled to remove any involatile fractions (in vacuo at room temperature) and subsequently analysed by ^{1}H, ^{13}C and ^{125}Te NMR as well as by GC-MS. ^{1}H NMR spectra have been reported for all of the C$_8$ products [12–14] obtained and ^{13}C NMR data are available for meso- and rac-3,4-dimethylhexa-2,5-diene [14].

3. Results and discussion

3.1. Synthesis

Basic aqueous solutions of Na$_2$Te react with bromobut-2-ene to give a product of stoichiometry $(MeCH=CHCH_2)_2Te$. ^{125}Te studies (Table 1) show that the product is a mixture of three compounds, which are readily identified from the ^{1}H and ^{13}C NMR (Table 1) as compounds 1–3 differing only with respect to the geometry about the double bonds. Integration of the ^{1}H or ^{127}Te NMR signals indicates that the E stereo-

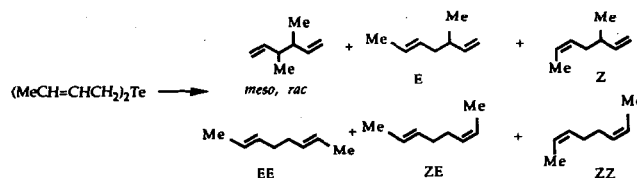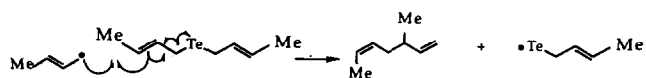chemistry around the double bond is favoured by a factor of 3 over the Z stereochemistry. Somewhat surprisingly, using 3-chlorobut-1-ene, an identical product is produced rather than the expected $(CH_2=CHCH(Me))_2Te$. Since the reactions are carried out in basic solutions and since allyl cations are stable, it seems likely that the mechanism of formation of the products involves the formation of the butenyl cation. Because of the electron donating effect of the methyl group, it might be expected that nucleophiles should attack on the CH$_2$ end of the allyl group and this is also likely to be favoured on steric grounds. Overall, it appears that attack of Te^{2-} at this end is exclusively favoured over attack at the other end. These reactions are outlined in Scheme 2.

3.2. Decomposition studies

Decomposition of $(MeCH=CHCH_2)_2Te$ in the liquid or the gas phases produces a mixture of compounds which have been identified by GC-MS and by ^{1}H and ^{13}C NMR as 2,4-dimethylhexa-1,5-diene, Z- and E-3-methylhepta-1,5-diene and ZZ-, ZE- and EE-octa-2,6-diene (Scheme 3) in the ratios shown in Table 2. In addition, small amounts of but-2-ene and unidentified (possibly aldehydic) products are observed. At lower temperatures, the liquid phase decomposition gives the same products but additionally some undecomposed $(MeCH=CHCH_2)_2Te$ is recovered. Significantly, no evidence is obtained for the formation of products containing (CH$_2$=CHCHMe)Te groups.

Scheme 2. Proposed mechanism for formation of $(Me_2CH=CHCH_2)_2Te$ from $MeCH=CHCH_2Br$ or $CH_2=CHCHMeCl$: (i) NaOH; (ii) Na$_2$Te.

Scheme 3. Products obtained from decomposition of $(MeCH=CHCH_2)_2Te$.

Scheme 4. Possible mechanisms for formation of allyl dimers involving radical attack on the double bond of a coordinated allyl group. 3,4-Hexa-1,5-diene can also be formed by this mechanism.

The observation of the full range of dimers of the 1-methylallyl radical is clearly inconsistent with a reductive coupling mechanism since the only products from $(MeCH=CHCH_2)_2Te$ would be expected to be ZE- and EE-octa-2,6-diene unless some reorientation of the allyl group occurred on a time scale faster than decomposition. However, if this were the case, some $(CH_2=CHCHMe)Te$ containing compounds would be expected under conditions of partial decomposition. Since none of this type of compound is observed, we conclude that reductive coupling is not a viable mechanism for this type of decomposition reaction.

Another possibility, particularly for reactions carried out in the liquid phase, involves homolytic cleavage of a Te–C bond followed by attack of the liberated allyl radical on the double bond of an existing $(MeCH=CHCH_2)_2Te$ molecule as shown in Scheme 4. This would lead directly to coupled products but only to 3,4-dimethylhexa-1,5-diene and isomers of 3-methyl-hepta-1,5-diene. The observation of substantial amounts of octa-2,6-diene is clearly incompatible with this mechanism.

The generation and coupling of 1-methylallyl radicals on the other hand would be expected to lead to a mixture of head-to-head, head-to-tail and tail-to-tail products as is indeed observed. The exact ratios of these products is difficult to predict but it might be expected marginally to favour the octa-2,6-dienes on the basis of steric effects which are known to be of importance in radical coupling reactions.

Detailed analysis of the NMR spectra of the various products (see Tables 2 and 3) from the liquid phase decomposition of $(MeCH=CHCH_2)_2Te$ indicates that

the ratio of head-to-head (octa-2,6-diene), head-to-tail and tail-to-tail dimers is 2.9 : 3.4 : 1. This ratio can be explained if the reactivity ratio in the coupling reaction is 0.37 : 0.63 with coupling of the less sterically hindered but-2-enyl radical being favoured over the 1-methylpropenyl radical. Since the product distribution can be fitted to simple statistics, it is evident that pathways other than the free radical one do not operate to a significant extent since these would invariably alter the product distribution so that it could not be fitted by a simple statistical model.

Although NMR analysis of the products (Table 2) indicates that there is very little difference in the product distribution between liquid or gas phase decomposition, GLC analyses (Table 3) suggest that there may be a slightly higher preference for the 3,4-dimethylhexa-1,5-diene products over the octa-2,6-dienes in the liquid phase. In all cases, E isomers are preferred to Z, by a factor of ca. 1.5 : 1. Also shown in Table 3 are the results of decomposition of $(MeCH=CHCH_2)_2Zn$, which has been reported to proceed via a free radical mechanism at temperatures above 100°C [15]. The overall yield of C_8 products, as well as their distribution, is remarkably similar to those observed in this study, and for the zinc alkyl, a greater preference for E isomers of the products was observed [15].

We have previously proposed that exchange of alkyl groups between tellurium centres in reactions of R_2Te with R'_2Te to give the unsymmetrical dialkyls $(RTeR')$ occurs via a radical chain process and have provided evidence for this in the liquid phase rearrangement of dihexenyltellurium to bis(cyclopentylmethyl)tellurium [11].

Since we are proposing that $(MeCH=CH_2CH)_2Te$ undergoes homolytic cleavage of the Te–C bond, the but-2-enyl radical so formed will attack the Te centre of another molecule of R_2Te to give R_3Te which will then liberate R $(R = MeCH=CH_2CH)$. The stereochemistry about the double bonds in the recovered R_2Te will then be determined by preferences in the radical attack rather than preferences existing in the

TABLE 3. Products from pyrolysis of $(MeCH=CHCH_2)_2Te/\%$ of C_8 fraction [a]

Phase	T (°C)	Conversion (%)	3,4-Dimethylhexa-1,5-diene		3-Methylhepta-1,5-diene		Octa-2,6-diene		
			meso	rac	E	Z	EE	ZE	ZZ
Liquid	165		6.7 [b]	13.5 [b]	29.2	20.4	9.7	15.7	4.7
Gas	350		7.3	8.9	29.3	20	11.2	17.2	6.1
$(CH_3CH=CHCH_2)_2Zn$ [c]	100		7.7	8.2	26.6	18.9	12.1	18.8	7.4

[a] Estimated from GLC ($\pm 10\%$). [b] Peaks overlap so rac is overestimated. rac and meso peaks arbitrarily assigned. [c] From ref. 15.

original alkyl. Apparently, as with the carbocations, the but-2-enyl radical always attacks the tellurium centre such that the products have CH_2 rather than CHMe bonded to the metal. Little or no change in the stereochemistry about the double bond occurs as a result of this radical chain reaction.

4. Conclusion

Since the decomposition of $(MeCH{=}CHCH_2)_2Te$ gives a mixture of 3,4-dimethylhexa-1,5-diene, E- and Z- 3-methyl-hepta-1,5-diene and EE-, EZ- and ZZ-octa-2,6-diene on decomposition in the gas or liquid phases, we conclude that this compound and, by analogy, other diallyltellurium compounds, decomposes via a mechanism involving homolytic fission of the Te–C bond followed by radical coupling reactions. We are currently studying the effect of co-decomposition of this compound with Me_2Cd in order to discover whether or not the dialkyl cadmium alters the decomposition process.

Acknowledgement

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