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Pyrolysis Pathways of Symmetrical and Unsymmetrical Organotellurium(II) Compounds

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Pyrolytic decompositions of ^{i}Pr$_2$Te, ^{t}Bu$_2$Te, (allyl)$_2$Te, (2-methylallyl)$_2$Te, and (3-methyl-3-butenyl)$_2$Te were investigated by using a combination of gas chromatography and gas chromatography/mass spectroscopy. Product distributions suggested that several competing pathways were operating. Evidence for tellurium–carbon bond homolysis was observed through variable-concentration and trapping experiments. A β-hydrogen elimination pathway was proposed to account for the observation of 2-methyl-2-propanetellurol and di-*tert*-butyl ditelluride in the pyrolysis of (^{t}Bu)$_2$Te. Both ^{i}PrTeH and diisopropyl ditelluride were observed during pyrolysis of ^{i}Pr$_2$Te. Substituted hexadienes were the predominant product in the pyrolytic decomposition of allyltellurium compounds. The observation of three isomeric dienes during decomposition of (3-methyl-3-butenyl)$_2$Te was inconsistent with an intramolecular pathway, suggesting a bond homolysis pathway for all three allyltellurium complexes. By comparison, decomposition of diallyl selenide yields propene as the major product. An "ene" pathway was proposed to account for these observations. Gas-phase pyrolytic decomposition of a series of unsymmetrical tellurium, MeTeR for R = allyl, 2-methylallyl, *tert*-butyl, and benzyl, led to the formation of MeTeTeMe and MeTeMe as the only observed Te-containing products. Radical coupling products, 1,5-hexadiene, 2,5-dimethylhexadiene, and bibenzyl, were the only observed organic products. Decomposition proceeded by bond homolysis; MeTe$^\bullet$ and R$^\bullet$ were generated. Evidence for a competing β-hydrogen elimination pathway was observed in the decomposition of MeTu^{t}Bu. The product distributions from the thermal decomposition of the unsymmetrical tellurium compounds were inconsistent with symmetrization prior to decomposition.

Introduction

Mercury cadmium telluride (Hg$_x$Cd$_{1-x}$Te, x = 0–1) holds great promise for application as infrared detectors in automobile engines and for night vision.[1] The chemical vapor deposition (CVD) of Hg$_x$Cd$_{1-x}$Te from organometallic precursors has potential for large-scale deposition of the uniform, thin films required for device manufacture.[2] The introduction of new alkyltellurium source reagents has led to improvements in growth rates and a decrease in the growth temperature.[3]

In a recent paper by Hoke et al.,[4] the effect of the alkyltellurium structure on the growth temperature of tellurium alloys was discussed. These authors proposed a simple bond homolysis model for decomposition of alkyltelluriums shown in reaction 1. The increase in the

$$\mathrm{RTeR} \xrightarrow{k_1} \{\mathrm{RTe}^\bullet + {}^\bullet\mathrm{R}\} \xrightarrow{k_2} \mathrm{R}^\bullet + \mathrm{Te} \qquad (1)$$

stability of the organic fragment produced upon homolysis correlated with the observed decrease in growth temperature for the series diethyl telluride, diisopropyl telluride, di-*tert*-butyl telluride, and diallyl telluride. It was presumed that the rate of decomposition of the tellurium-centered radical was faster than the the initial bond homolysis, i.e., $k_2 > k_1$. While these reagents showed improvement in the decomposition temperature, volatility was sacrificed.

An approach to more volatile tellurium source reagents is to prepare unsymmetrical tellurium alkyls in which one ligand has a low molecular weight, while the second has a weak Te–C bond, which contributes to facile, low-temperature decomposition. An example is methylallyltellurium, which is more volatile than diallyltellurium yet would be predicted to have similar decomposition kinetics. Based on the Hoke model, bond homolysis of the tellurium–allyl bond is thought to be preferred, and the resulting methyltellurium radical should have a transient existence. For example, if $k_1 \gg k_2$ in reaction 1, then the rate of decomposition of the organotellurium is determined by k_1 and the strength of the Te–R′ bond.

Tutt et al. recently proposed that prior to decomposition, ligand redistribution occurred to form symmetrical dialkyltellurium derivatives (reaction 2).[5] Their experiments

$$2\mathrm{MeTeR} \rightarrow \mathrm{MeTeMe} + \mathrm{RTeR} \qquad \mathrm{R} = \text{allyl, } \textit{tert}\text{-butyl} \qquad (2)$$

were based on differential scanning calorimetry, which unfortunately did not allow direct spectroscopic observation of the products of redistribution.

As part of our effort to develop new tellurium source reagents for the MOCVD growth of tellurium-containing alloys, we decided to study the decomposition of a series of symmetrical and unsymmetrical dialkyltelluriums. We began an investigation of the gas-phase decomposition chemistry of alkyltellurium compounds to test the models in reactions 1 and 2 and quickly discovered that the reaction pathways were more complex. In this paper, we report the results of our preliminary study on the pyrolytic decomposition of the symmetrical and unsymmetrical organotellurium(II) compounds. Included in this study were ^{i}Pr$_2$Te, ^{t}Bu$_2$Te, (allyl)$_2$Te, (2-methylallyl)$_2$Te, (3-methyl-3-butenyl)$_2$Te, diallyl selenide, and the unsymmetrical compounds of formula MeTeR, where R = allyl, 2-methylallyl, benzyl, or *tert*-butyl, and ^{t}BuTe(allyl).

Experimental Section

Synthesis of Tellurium Compounds. Dimethyl telluride, diisopropyl telluride, di-*tert*-butyl telluride, and diallyl selenide were prepared by literature methods.[6,7] A slightly different

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synthesis of diallyl telluride has been reported.[8] The synthesis of 2-methyl-2-propanetellurol (^{t}BuTeH) from methanolysis of ^{t}BuTeSiMe$_3$ has been reported.[9] The synthesis of bis(2-methylallyl)tellurium, bis(3-methyl-2-butenyl)tellurium, methylallyltellurium, *tert*-butylmethyltellurium, methylbenzyltellurium, *tert*-butyallyltellurium, and methyl(2-methylallyl)tellurium are described below. All manipulations were carried out under an argon or nitrogen atmosphere. All of the compounds studied are dense, volatile, yellow, orange, or red colored, extremely pungent, air- and light-sensitive liquids, which were purified by distillation under reduced pressure. Purity was assessed by a combination of gas chromatography, mass spectrometry, and multinuclear NMR spectroscopy. 2,2′-Azoisobutane were purchased from Alfa and 1,1′-azo-2-propene was prepared by substitution of allyl chloride for allyl benzenesulfonate in the literature procedure.[10] ^{1}H and ^{125}Te NMR spectra were recorded on a Bruker WP200SY spectrometer using a VSP 200 broad-band probe. Chemical shifts are given in parts per million and are referenced to tetramethylsilane (^{1}H) and to di-*tert*-butyl telluride (^{125}Te at δ 990). Elemental analyses were performed by Galbraith Laboratories.

Diallyl Telluride. Tellurium powder (14 g, 0.11 mol) was slurried in 50 mL of degassed, distilled water. A solution of NaBH$_4$ (12.5 g, 0.33 mol) in 75 mL of degassed, distilled water was added by cannula over a 1-h period. The temperature rose rapidly (to between 40 and 50 °C) after a short induction period, accompanied by the evolution of gas. The slurry of the grey or black tellurium metal began to turn purple, the characteristic color of Te$_2^{2-}$. When approximately half of the borohydride solution was added, the temperature no longer increased significantly, but gas continued to be evolved rapidly. Accomodation of the large volume of hydrogen produced in this reaction required either slow addition of the reductant, cooling of the reaction vessel, or use of a large-bore gas inlet to vent the gas. When addition of the second equivalent of NaBH$_4$ solution was complete and gas evolution had ceased, a virtually colorless solution was observed. Aqueous NaOH (18 mL, 6 M, 0.11 mol) was added to the solution. Allyl bromide (19 mL, 26.6 g, 0.22 mol) was added dropwise at 0 °C over a 1-h period. The reaction mixture turned yellow as the alkylation proceeded. The organic product was dispersed as oily droplets in the rapidly stirred solution. After addition was complete, the solution was allowed to warm to room temperature and was stirred overnight. The mixture was extracted with ether (4 × 50 mL) and the ether layer dried over magnesium sulfate. The ether was evaporated and the crude yellow product distilled (40–42 °C (0.1 Torr), 16 g, 70% yield based on Te metal). Diallyl telluride was isolated as a yellow oil, which darkened upon prolonged exposure to light. ^{125}Te NMR (C$_6$D$_6$) δ 378 ppm.

Bis(2-methylallyl) Telluride. A solution of NaBH$_4$ (12.5 g, 0.33 mol) in 100 mL of degassed, distilled water was slowly added to a magnetically stirred slurry of tellurium powder (−100 mesh, 16 g, 0.125 mol) in 100 mL of water under nitrogen at room temperature over 3–4 h. When addition was complete, a solution of aqueous NaOH (42 mL, 6 M, 0.25 mol) was added, causing a slight discoloration of the previously colorless solution to a light purple color. The mixture was cooled to 0 °C and 2-methylallyl chloride (25 mL, 0.25 mol) was added slowly. The solution was warmed to 10 °C, whereupon formation of a yellow oil was observed on top of the aqueous layer. The mixture was stirred at room temperature for 90 min and extracted with 1 × 100 and 5 × 50 mL of diethyl ether. The combined ether extracts were dried over anhydrous MgSO$_4$. The ether was removed by distillation at atmospheric pressure and the residue distilled under vacuum to yield bis(2-methylallyl) telluride (50–55 °C (0.15 Torr), 14.8 g, 50% yield based on Te metal) as a yellow oil. The yellow oil was air-sensitive and turned more orange upon exposure to room light with no detectable change in purity as observed by GC. Anal. Calcd for C$_8$H$_{14}$Te: C, 40.41; H, 5.93. Found: C, 40.75; H, 5.92. ^{125}Te NMR (C$_6$D$_6$) δ 358 ppm.

Bis(3-methyl-3-butenyl) Telluride. In a procedure similar to the synthesis of diallyl telluride, a solution of NaBH$_4$ (3 g, 0.08 mol) in 30 mL of degassed, distilled water was slowly added to a magnetically stirred slurry of tellurium powder (−100 mesh, 4 g, 0.125 mol) in 30 mL of water under nitrogen at room temperature. Aqueous NaOH (11 mL, 6 M, 0.066 mol) was added and the solution cooled to 0 °C. 4-Bromo-2-methyl-2-isobutene (10 g, 0.067 mol) was added. After it was stirred at room temperature for 1 h, the solution was extracted with 4 × 25 mL of ether and worked up as described for diallyl telluride. Distillation at reduced pressure gave bis(3-methyl-3-butenyl) telluride (65–70 °C (0.2 Torr), 5.7 g, 69% yield based on Te metal) as a yellow oil. Anal. Calcd for C$_{10}$H$_{18}$Te: C, 45.18; H, 6.83. Found: C, 45.19; H, 6.77. ^{125}Te NMR (C$_6$D$_6$) δ 391 ppm.

Methylallyltellurium. Methyllithium (44.5 mL, 1.4 M, 0.062 mol) in ether was added to a slurry of tellurium powder in 30 mL of THF at −78 °C. The grey slurry was allowed to warm slowly. As the reaction proceeded, the tellurium powder was consumed. The yellow solution was alkylated with allyl chloride (5.2 mL, 0.063 mol) at 0 °C. Solvent was evaporated under a nitrogen stream and the product distilled under vacuum to yield methylallyltellurium (40 °C (12 Torr), 4.7 g, 40% yield based on Te metal). ^{125}Te (C$_6$D$_6$) δ 182 ppm.

Methyl-*tert*-butyltellurium. *tert*-Butyllithium (37.5 mL, 1.7 M, 0.063 mol) in pentane was added to a slurry of Te powder (8 g, 0.063 mol, −200 mesh) at −78 °C in 50 mL of THF. The solution began to turn yellow almost immediately, but the bulk of the Te was consumed as the mixture slowly warmed. Methyl iodide (3.9 mL, 0.063 mol) was added to the transparent yellow solution. A white precipitate was observed and the solution acquired a greenish yellow tinge. The solution was filtered and the solvent partially removed from the filtrate under a stream of nitrogen. The remaining solution was fractionally distilled under vacuum twice to yield methyl-*tert*-butyltellurium (40 °C (0.25 Torr), 1.6 g, 13% yield) as a yellow liquid. ^{125}Te NMR (C$_6$D$_6$) δ 497 ppm.

Methylbenzyltellurium. Methyllithium (23 mL, 1.8 M, 0.041 mol) in ether was added to a slurry of tellurium powder (5.292 g, 41.47 mmol) in 30 mL of THF at −78 °C under argon in a flask wrapped with aluminum foil. The solution initially turned deep red then light yellow as the addition was completed. After the LiTeMe solution was stirred for 2 h at 0 °C, a solution of benzyl bromide (4.9 mL, 41.5 mmol) in 5 mL of THF was added dropwise. The light yellow solution was warmed to room temperature slowly and stirred overnight. The solution was filtered and the precipitate was washed with 20 mL of hexane. The solvent was fractionally distilled away under reduced pressure, and the product (7.83 g, 81% based on Te metal) was collected as a malodorous yellow liquid at 60–63 °C (0.15 Torr). Anal. Calcd for C$_8$H$_{10}$Te: C, 41.10; H, 4.31. Found: C, 41.57; H, 4.59. ^{125}Te NMR (C$_6$D$_6$) δ 314 ppm.

***tert*-Butylallyltellurium.** To a slurry of Te powder (50 g, 391.8 mmol) in 200 mL of THF (distilled from sodium benzophenone), at −25 °C, ^{t}BuLi (232 mL, 1.7 M in pentane, 394 mmol) was added dropwise with stirring under purified argon in an aluminum-foil-wrapped flask. The solution turned deep red then yellow-green as the addition was completed. The solution was then stirred at 0 °C for 30 min and a solution of allyl bromide (35.0 mL, 404 mmol) was added dropwise at 0 °C. The light yellow solution was stirred 12 h in the dark, cooled to −78 °C, and filtered. The precipitate was washed with three portions of 25 mL of hexane. The filtrate and washings were combined and the solvents were removed by fractional vacuum distillation around 40 °C. The crude product was then collected in a −198 °C trap. Traces of solvent were again vacuum distilled and the product (63.6 g, 282 mmol, 72% yield based on Te metal) was collected at 39–40 °C (3 Torr) as an air- and light-sensitive yellow liquid. Anal. Calcd for C$_7$H$_{14}$Te: C, 37.24; H, 6.25; Te, 56.51. Found: C, 37.25; H, 6.24; Te, 56.83. ^{125}Te NMR (C$_6$D$_6$) δ 717 ppm.

Methyl(2-methylallyl)tellurium. Methyllithium (70 mL, 1.4 M, 0.1 mol) in diethyl ether was added by cannula to a slurry of Te powder (12.8 g, 0.1 mol) in 200 mL of THF under nitrogen at −78 °C. The solution was allowed to stir while slowly warming to room temperature. After several hours, a transparent, light yellow solution was observed. The solution was again cooled to −78 °C, and 3-chloro-1-propene (10 mL, 0.1 mol) was added by syringe over a 15-min period. The light yellow solution began to darken to a more reddish color almost immediately. The solution was allowed to warm to room temperature, yielding a brown, but transparent, solution. Solvent was removed under

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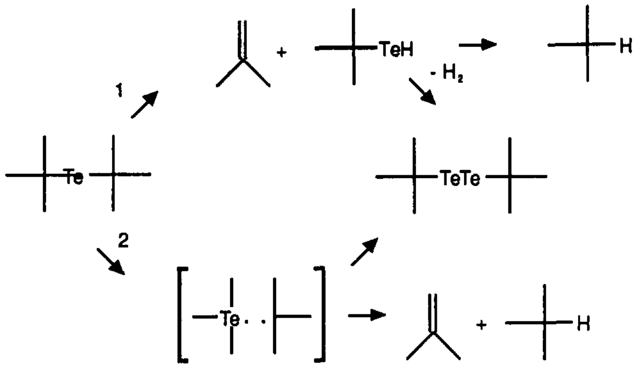
Scheme I. Proposed Pathways for Decomposition of ^{t}Bu$_2$Te



vacuum followed by distillation of methyl(2-methylallyl)tellurium (40–43 °C (0.2 Torr), 8.75 g, 44% yield based on Te metal) as a yellow oil. Elemental analysis was unsatisfactory because of the compound's instability. ^{125}Te NMR (C$_6$D$_6$) δ 215 ppm.

2-Methyl-2-propanetellurol. *tert*-Butyl lithium in pentane (18 mL, 1.7 M, 0.031 mol) was added to a slurry of Te powder (4 g, 0.032 mol, −200 mesh) in 20 mL of THF at −78 °C. After several hours at −78 °C, the mixture was allowed to warm to 0 °C. Chlorotrimethylsilane (4 mL, 3.4 g, 0.03 mol) was added to the yellow solution, yielding an orange solution and a white precipitate. This mixture was filtered and the solvent evaporated overnight under a nitrogen stream through a bleach trap. An extremely foul smelling product (1.5 g) was collected after filtration. ^{1}H NMR and GC/MS indicated that ^{t}BuTeSiMe$_3$ had been formed along with a small amount of (^{t}Bu)$_2$Te. Treatment of the crude mixture of ^{t}BuTeSiMe$_3$ with methanol followed by vacuum transfer of the volatiles allowed isolation of a solution of ^{t}BuTeH in MeOSiMe$_3$ by GC/MS. The new ^{1}H NMR (C$_6$D$_6$) resonance at −3.37 ppm was in the range expected for a Te–H resonance.

Pyrolysis Studies. The pyrolyses were conducted by using the injection port of a Hewlett-Packard HP5890A gas chromatograph (GC) as the pyrolysis chamber. The volatile products passed immediately into the GC and were separated on a 60-m poly(methylphenyl)silicone column. The products were identified on a Hewlett-Packard HP5970 mass spectrometer (MS). Quantitative studies were carried out by decomposition on a Perkin-Elmer Sigma 2000 gas chromatograph on a 30-m poly(methylphenyl)silicone column equipped with a LCI-100 integrator. Typically, 0.5-μL samples were injected. The products were also identified by comparison of retention times and fragmentation patterns with those of authentic samples.

A Lindberg decomposition furnace in conjunction with a Perkin-Elmer Sigma 2000 GC was also used to study the thermal decompositions of the tellurium compounds. With this system, compounds were delivered into a decomposition furnace with a nitrogen carrier gas. Volatile reaction products from the decomposition were then carried to the GC and injected onto the column by using a gas sampling valve. The volatile components of the decomposition were identified by comparing their retention times with those of authentic samples. Confirmation was achieved by withdrawing samples for gas chromatography/mass spectrometry (GC/MS).

Results and Discussion

Symmetrical Tellurium Compounds. Pyrolysis of di-*tert*-butyl telluride (^{t}Bu$_2$Te) at 400 °C resulted in complete decomposition of the parent compound and produced 95–99% of a 1:1 mixture of isobutane and isobutene. The ratio of isobutane to isobutene was invariant to the pyrolysis temperature over the temperature range 300–450 °C. The remaining 1–5% of products were not identified; however, 2,2,3,3-tetramethylbutane was not detected in these experiments. Two pathways were considered to account for the observed products as shown in Scheme I.

Pyrolysis of benzene solutions of ^{t}Bu$_2$Te at 400 °C showed a concentration dependence of the isobutane to isobutene ratio (Table I, entries 1–5) consistent with pathway 2, Scheme I. As the concentration of *tert*-butyl radicals decreased, the unimolecular fragmentation to isobutene was expected to be favored over bimolecular processes leading to isobutane. The observed decrease in the isobutane to isobutene ratio was consistent with pathway 2.

Table I. Product Distribution in the Pyrolysis[a] of Di-*tert*-butyl Telluride

^{t}Bu$_2$Te concn	area, %		ratio
	C$_4$H$_{10}$	C$_4$H$_8$	C$_4$H$_{10}$/C$_4$H$_8$
1. 100%	46.3	50.4	0.92
2. 50% in benzene	46.5	53.2	0.87
3. 10% in benzene	44.1	55.1	0.80
4. 5% in benzene	35.9	61.3	0.59
5. 1% in benzene	34.8	60.1	0.58
6. 10% in 1,4-cyclohexadiene	53.3	46.5	1.2
7. 5% in 1,4-cyclohexadiene	63.2	36.7	1.7
8. 1% in 1,4-cyclohexadiene	59.6	33.8	1.8

[a] Column = 40 °C, injector = 400 °C, detector = 250 °C.

Copyrolysis of ^{t}Bu$_2$Te in 1,4-cyclohexadiene (a source of hydrogen atoms,[11] Table I, entries 1 and 6–8) showed a corresponding increase in the isobutane/isobutene ratio, consistent with the trapping of ^{t}butyl radicals by the solvent. Similar results have been observed in the pyrolysis of *tert*-butylphosphine.[12]

Azoalkanes are believed to decompose exclusively through formation of hydrocarbon radicals. Two studies have been reported in the literature[13,14] for the pyrolysis of 2,2′-azoisobutane, with surprisingly different results. In the earliest study by Levy and Copeland, greater than 90% of the products of the pyrolysis of 2,2′-azoisobutane in a sealed bulb were isobutane and nitrogen. Only small amounts of 2,2,3,3-tetramethylbutane were observed. The absence of isobutene was attributed to the reaction of *tert*-butyl radicals with isobutene to form isobutane and methylallyl radicals. The methylallyl radicals were presumed to have polymerized to give the brown film deposited on the walls of the reaction vessel. Blackman and Eatough observed a 1:1 mixture of isobutene to isobutane from the pyrolytic decomposition of 2,2′-azoisobutane in a flow system. Although they observed a 1:1 mixture, the C$_4$ products accounted for only 60% of the *tert*-butyl radicals. It was presumed, but not demonstrated, that the fate of the remaining *tert*-butyl radicals was formation of 2,2,3,3-tetramethylbutane. During our study, one additional report of the pyrolysis of 2,2′-azoisobutane appeared in the literature.[15] Gladfelter et al. reported 10% 2,2,3,3-tetramethylbutane from pyrolysis of 2,2′-azoisobutane at 425 °C and 700 Torr (along with 53% isobutene and 37% isobutane). As the pressure decreased and the pyrolysis temperature increased, more 2,2,3,3-tetramethylbutane was detected. The differing product distributions in these three reports suggested that the nature and ratio of the products depended on temperature, pressure, carrier gas, and solvent.

Given the different observations in these literature reports, 2,2′-azoisobutane was pyrolyzed in the injection port of the GC/MS under conditions analogous to those used in the pyrolysis of ^{t}Bu$_2$Te. Pyrolysis of pure 2,2′-azoiso-

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Table II. Isobutane/Isobutene Ratio from Pyrolysis of Azoisobutane in 1,4-Cyclohexadiene[a]

	isobutane/isobutene ratio		
injector temp, °C	100%	10%	1%
300	50:50	96:4	98:2
350	47:53	91:9	96:4
450	46:54	89:11	92:8

[a] Column = 60 °C, detector = 250 °C.

butane at 350 °C in the GC/MS failed to produce detectable amounts of 2,2,3,3-tetramethylbutane. Isobutane and isobutene were observed as the major products. The results of pyrolysis for solutions of 2,2′-azoisobutane in 1,4-cyclohexadiene are summarized in Table II. Several conclusions can be drawn from the data in Table I. In the absence of the trapping agent, the isobutane/isobutene ratio appeared to be largely independent of temperature in the range 300–450 °C. At constant temperature, the isobutane/isobutene ratio increased as the concentration of the azo compound decreased. The 98:2 isobutane/isobutene ratio observed at 300 °C for pyrolysis of a 1% solution of $C_8H_{18}N_2$ in cyclohexadiene corresponded to virtually complete trapping of the *tert*-butyl radical! At constant 2,2′-azoisobutane concentration, the ratio of isobutane/isobutene decreased as the temperature increased. Increased thermal decomposition of the cyclohexadiene to benzene at higher temperature appeared to have the effect of reducing the concentration of the trapping agent. In comparing the data from Tables I and II, the isobutane/isobutene ratio for a given concentration of 2,2′-azoisobutane was much higher than those in Table I for tellurium compounds. The difference in isobutane/isobutene ratio observed in the pyrolysis of di-*tert*-butyl telluride and 2,2′-azoisobutane, especially in the presence of a radical trap, suggested that another reaction pathway was accessible to the tellurium compound.

Data in Tables I and II were consistent with bond homolysis as the dominant pathway in the pyrolysis of $(^tBu)_2Te$. Nevertheless, careful control of the pyrolysis (injection port) and column temperatures led to the detection of small amounts of both 2-methyl-2-propanetellurol (^tBuTeH, 4%) and di-*tert*-butyl ditelluride ($^tBuTeTe^tBu$, 0.1%). Independent synthesis of ^tBuTeH and subsequent pyrolysis revealed that isobutane was the primary decomposition product from 2-methyl-2-propanetellurol. Pyrolysis of di-*tert*-butyl ditelluride[16] gave a mixture of isobutane and isobutene in a ratio similar to that obtained from pyrolysis of $^tBu_2Te$. The formation of $^tBu_2Te$ was also observed, circumstantial evidence that decomposition of the ditelluride occurred by extrusion of Te and formation of $^tBu_2Te$. The tellurium extrusion pathway has been previously proposed for the decomposition of both dimethyl and dibenzyl ditelluride.[17,18] The formation of $^tBuTeTe^tBu$ and ^tBuTeH by coupling of $^tBuTe^\bullet$ radicals and $H^\bullet$ abstraction by $^tBuTe^\bullet$ were also consistent with the bond homolysis pathway. The ditelluride formation pathway requires that the alkyltellurium radicals are sufficiently long-lived to undergo dimerization. *In reaction 1, k_2 is not necessarily greater than k_1.*

Small quantities of ^iPrTeH and $^iPr_2Te_2$ was observed in the pyrolysis of $^iPr_2Te$ at 350 °C by GC/MS. Only small amounts of hexanes were detected, with the majority of the products identified as C_3 hydrocarbons. We were unable to separate and identify the components of the C_3 fraction, although, by analogy to $^tBu_2Te$ decomposition, both propane and propene were expected.

To test the intermediacy of tellurols in the formation of ditellurides during decomposition of organotellurium compounds, the gas-phase pyrolysis of Me_2Te was investigated. Dimethyl ditelluride had been independently verified to have sufficient stability under the reaction conditions to be detected by GC/MS. Unfortunately, dimethyl telluride did not appear to decompose. The thermal stability of dimethyl telluride was consistent with the observed trends for alkyl tellurium compounds with primary, secondary, and tertiary alkyl groups.[4]

In light of the complete trapping of *tert*-butyl radicals generated from 2,2′-azoisobutane in 1,4-cyclohexadiene, the incomplete trapping of *tert*-butyl radicals by 1,4-cyclohexadiene in the decomposition of $^tBu_2Te$ was puzzling. It was possible that the relative rates of homolysis of the Te–C bond, diffusion of the carbon radical from the radical pair cage, and disproportionation to isobutene prevented complete trapping of the ^tBu radicals by 1,4-cyclohexadiene. If pyrolysis in the injection port of the GC occurred prior to volatilization of the reactant and abstraction of $H^\bullet$ by $^tBuTe^\bullet$ from $^tBu^\bullet$ in the radical cage were faster than diffusion from the cage, then incomplete trapping would be observed. However, the lifetime of radical cages in a gas-phase reaction is vanishingly small. Our observation of identical results in the GC injector port and in the continuous flow system permit us to discount the possibility that radical cage reactions contributed to the failure of 1,4-cyclohexadiene to trap the ^tBu radicals.

Another possible reaction pathway consistent with the formation of ^tBuTeH, isobutene, and isobutane form $(^tBu)_2Te$ was a β-hydrogen elimination. A β-hydrogen elimination pathway would require an empty, low-energy orbital of the proper symmetry on the tellurium to mediate the hydrogen transfer. Indeed, the classic β-hydride elimination pathway in both main-group and transition-metal organometallic compounds involves transfer of a β-hydride (H^-) to an empty orbital (e.g., Et_3Al decomposition to Et_2AlH and ethylene).[19] However, in group V and group VI organometallics (elements with lone pairs of electrons), elimination can occur via proton transfer to the lone pair followed by elimination of alkene. For example, the pyrolysis of methyl *tert*-butyl ether was observed to yield methanol and isobutene as 99% of the products in the temperature range 433–495 °C.[20] The lack of inhibition by added isobutene of the rate of decomposition argued for a unimolecular elimination with the four-centered transition state shown in reaction 3. As drawn, the transfer of the hydrogen in reaction 3 is distinct from the classic "β-hydride elimination" pathway in organotransition-metal chemistry. Similar data were obtained for the pyrolysis of $(^iPr)_2O$ and EtO^tBu.[20] Computer simulations of organotellurium pyrolysis showed that, for both $^tBu_2Te$ and $^iPr_2Te$, β-hydrogen elimination is not the dominant pyrolysis pathway, but it does play an important role in the decomposition of these organotellurium compounds.[21]

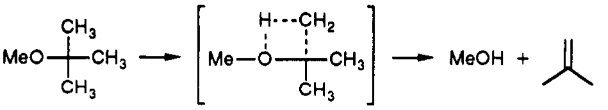

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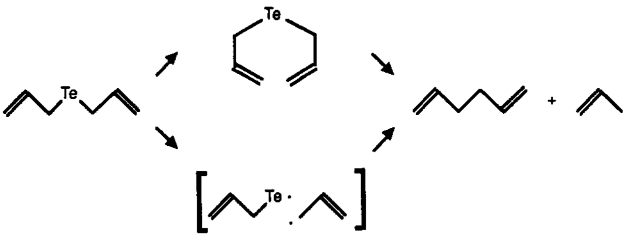
Table III. Product Distribution in the Pyrolysis[a] of Diallyl Telluride

$C_6H_{10}Te$ concn	area,[b] %	
	C_3H_6	C_6H_{10}
1. 100%	2.8	97.2
2. 50% in benzene	1.5	98.5
3. 10% in benzene	1.1	98.8
4. 1% in benzene	1.5	98.4
5. 1% in 1,4-cyclohexadiene	8.1	91.9
6. 0.1% in 1,4-cyclohexadiene	27	73.0

[a] Column = 40 °C, detector = 250 °C, injector = 400 °C. [b] Normalized by the number of carbon atoms.

Scheme II. Proposed Pathways for the Decomposition of (allyl)$_2$Te

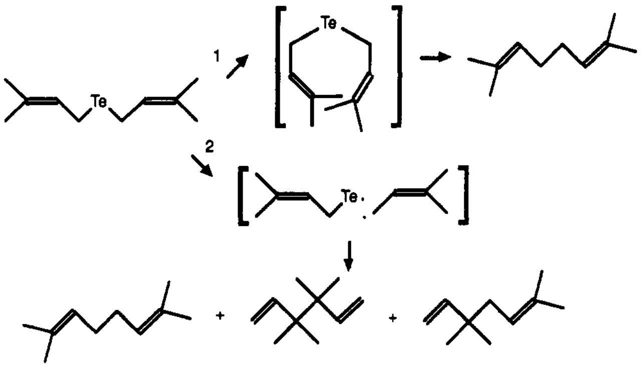


Pyrolysis of diallyl telluride above 300 °C led to complete decomposition of the organotellurium species and formation of 1,5-hexadiene and propene in a 97:3 ratio, again invariant with change in injector temperature. Similarly, pyrolysis of bis(2-methylallyl) telluride led to predominantly 2,5-dimethyl-1,5-hexadiene with very little isobutene being produced (97:3 at 400 °C). A slight concentration dependance of the diene to propene ratio during decomposition of diallyl telluride was observed in benzene as shown in Table III, entries 1–4. Very little trapping of allyl radicals was observed in a 1% solution of diallyl telluride in 1,4-cyclohexadiene. Only at very low concentrations (0.1%) of tellurium in cyclohexadiene were significant amounts of propene (27%) observed at 400 °C (entries 5 and 6).

In the absence of a H$^\bullet$ source, the product ratios were similar to those reported from gas-phase decomposition of the corresponding azo derivatives. The gas-phase thermal decomposition of 1,1′-azo-2-propene produced 1,5-hexadiene with less than 0.1% propene,[10] while diene products, exclusively, were observed in the pyrolyses of three isomeric methylallyl azo derivatives (*E*,*E*)-4,4′-azo-2-isobutene, (*Z*,*Z*)-4,4′-azo-2-isobutene, and 3,3′-azo-1-isobutene.[22] The same ratios of products were observed in each case, suggesting rapid isomerization of the 2-methylallyl radicals. Generation of 2-methylallyl radicals by addition of H$^\bullet$ to 1,3-butadiene at low temperature demonstrated that allylic–allylic radical reactions occurred exclusively by combination and not by disproportionation.[23] Superficially, these results were consistent with a bond homolysis pathway for the decomposition of diallyl telluride. Significant discrepancies were observed in the presence of a H$^\bullet$ source. In our studies, the pyrolysis of 1,1′-azo-2-propene in the presence of 1,4-cyclohexadiene at 400 °C led to 99% trapping of the allyl radicals as propene. These observations led to a consideration of alternative pathways to bond homolysis.

To test for an intramolecular pathway (Scheme II, top pathway), a 1:1 mixture (v/v) of (allyl)$_2$Te and (2-methylallyl)$_2$Te was pyrolyzed at 300 °C, leading to complete decomposition of the tellurium reagents and observation of a 1.5:1.8:1 ratio of 1,5-hexadiene, 2-methyl-1,5-hexadiene, and 2,5-dimethyl-1,5-hexadiene, respectively. The intramolecular decomposition of tellurium compounds by reaction 1 in Scheme III was predicted to yield very little 2-methyl-1,5-hexadiene, the coupled product of allyl and 2-methylallyl radicals. However, below 300 °C the product of ligand redistribution, allyl(2-methylallyl)tellurium, was also observed. This unsymmetrical organotellurium product was observed at temperatures as low as 90 °C, well below the decomposition temperature of either reagent! Similar ligand redistribution reactions were observed for mixtures of $^tBu_2Te$ with $^iPr_2Te$, (allyl)$_2$Te, and (2-methylallyl)$_2$Te. In each case, the unsymmetrical organotellurium(II) compound was observed along with the products resulting from combination of the two different alkyl radicals. The ligand exchange could arise from reversible addition of a hydrocarbon radical to the bis(organo)tellurium compounds, by interception of the hydrocarbon radical by a tellurium-centered radical or by a bimolecular reaction that does not involve bond homolysis.[24] Copyrolysis of diallyltellurium and 2,2′-azoisobutane yielded a mixture of hexadiene, isobutane, isobutene, and heptene. Up to 85% of the latter was detected during pyrolysis of a 1% solution (v/v) of tellurium in 2,2′-azoisobutane. Unreacted 2,2′-azoisobutane and tellurium were observed along with *tert*-butyl allyl telluride. There was no evidence to suggest the formation of the unsymmetrical azo compound $C_3H_5N{=}NCMe_3$.

Scheme III. Proposed Pathways for the Decomposition of Bis(3,3-dimethylallyl) Telluride



The decomposition of (3-methyl-2-butenyl)$_2$Te was selected as a further probe of intramolecular decomposition pathways for allyl-like tellurium derivatives. As illustrated in Scheme III, intramolecular decomposition (pathway 1) would lead exclusively to 3,3,4,4-tetramethyl-1,5-hexadiene, while a pathway involving substituted allyl radicals would produce a mixture of the products shown in pathway 2 (Scheme III), unless prior rearrangement of the starting material occurred. Pyrolysis of bis(3-methyl-2-butenyl) telluride at 350 °C yielded three compounds, which analyzed for the stoichiometry $C_{10}H_{18}$, consistent with pathway 2. The observed products could be accounted for by Te–C bond homolysis and isomerization of the dimethylallyl radical, followed by combination or by rapid isomerization of the starting material, followed by intramolecular decomposition. The isomerization of the starting material could occur by a 1,3-tellurium shift[25] or by recombination of tellurium radicals with an isomerized dimethylallyl radical. These reactions would have to be faster than the

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Scheme IV. Production of Propene via an Ene Reaction in the Thermal Decomposition of Diallylselenium

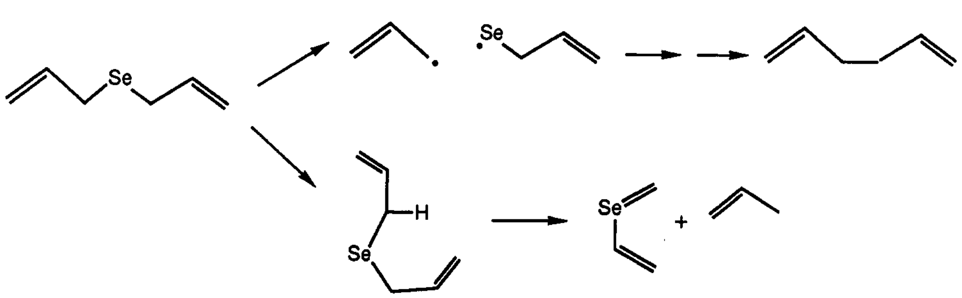


Table IV. Product Distribution in the Pyrolysis[a] of Diallyl Sellenide

	area,[b] %	
$C_6H_{10}Se$ concn	C_6H_{10}	C_3H_6
1. 100%	34	66
2. 50% in benzene	34	66
3. 1% in benzene	17	83
4. 1% in 1,4-cyclohexadiene	0	100

[a] Column = 40 °C, detector = 250 °C, injector = 400 °C. [b] Normalized by the number of carbon atoms.

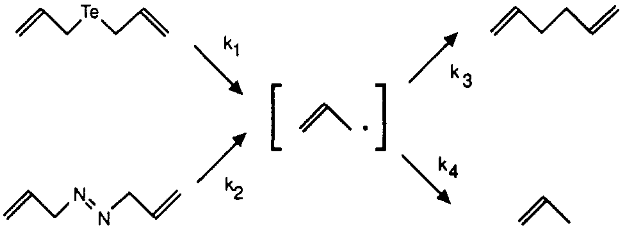
combination of two dimethylallyl radicals. No rearrangement of the starting material was detected by ^{125}Te NMR when a benzene-d_6 solution of the tellurium compound was heated at 80 °C for several hours. Taken together, the data argue against an intramolecular decomposition pathway for diallyl telluride.

For comparison, a series of analogous experiments were conducted on diallyl selenide. Several important differences between the two allyl chalcogenides and azopropene were observed. Much higher temperatures were required for the decomposition of diallyl selenide. As a neat liquid, propene was the *major* product upon pyrolysis of diallyl selenide rather than hexadiene as observed for diallyl telluride and azopropene under identical conditions (Table IV, entry 1). Copyrolysis experiments with 1,4-cyclohexadiene demonstrated that, under the same conditions (400 °C) and comparable concentrations (1% v/v), only 8% of the allyl radicals produced from tellurium were trapped by 1,4-cyclohexadiene (Table III)[26] while complete trapping was observed in the decomposition of $(allyl)_2Se$ and $(allyl)_2N_2$ (Table IV). It would appear that the decomposition of diallyl selenide is similar to that of 1,1′-azo-2-propene but differs from that of diallyl telluride.

A pathway related to the intramolecular decomposition in Scheme IV is the "ene" pathway, which involves a unimolecular six-member transition state.[27] Comparing the entire series of bis(allyl) derivatives of the chalcogenides, pyrolytic decomposition of diallyl ether yields propene and acrolein,[28] while pyrolysis of diallyl sulfide (at 390 °C) yields a mixture of propene and the transient species $CH_2{=}CHC({=}S)H$, which subsequently dimerizes.[29] The latter has been proposed to occur by the ene pathway.

While the ene pathway for the decomposition of diallyl selenide would account for the observation of propene during pyrolysis of neat diallyl selenide, the absence of propene, the weakness of the Te–C bond, and the instability of telluroaldehydes[30] (e.g., $CH_2{=}CHC({=}Te)H$) suggested little contribution from the ene pathway in the decomposition of tellurium. For diallyl selenide, the other product would be $CH_2{=}CHC({=}Se)H$, whose reactivity with 1,4-cyclohexadiene is not known. Competition between the ene and other pathways in the presence of 1,4-cyclohexadiene cannot be excluded.

Scheme V. Reactions of Allyl Radicals



The explanation most consistent with the observed results for the decomposition of $(C_3H_5)_2E$ (E = N_2 and Te) is a difference in the kinetics of bond homolysis in the series of compounds. This is illustrated in Scheme V. Both the rates of trapping (k_4) and the rate of dimerization (k_3) are independent of the source of allyl radicals. Since the dimerization and trapping of allyl radicals are both bimolecular processes, the relative amounts of hexadiene and propene will depend on the concentration of allyl radicals and thus on the rate of allyl radical generation. If $k_1 \gg k_2$, then the relative concentration of allyl radicals from diallyl telluride at a given temperature (and concentration of 1,4-cyclohexadiene) will be greater than that from 1,1′-azo-2-propene or diallyl selenide. The literature data on methallyl radical reactivity cited above[22,23] suggested that k_3 is greater than k_4. If $k_1 \gg k_3 \gg k_4$ for diallyl telluride, then the observed product ratio should favor the formation of hexadienes (i.e., k_3, k_4 are the rate-determing steps). If $k_3 > k_4 \gg k_2$, then k_2 becomes the rate-determining step and the product ratio will be dependent on the concentration of the trap (1,4-cyclohexadiene). This appears to be the case for both 1,1′-azo-2-propene and diallyl selenide. Further experiments are under way to explore the differences in reactivity between diallyltellurium, diallylselenium, and 1,1′-azo-2-propene.

Unsymmetrical Tellurium Compounds. The pyrolysis of MeTeR compounds (R = allyl, 2-methylallyl, *tert*-butyl, and benzyl) was characterized in all cases by the formation of dimethylditellurium, MeTeTeMe (major product), and dimethyltellurium, MeTeMe (minor product), as the only volatile tellurium-containing products and the coupled organic byproducts, R–R. Dimethyltellurium could be formed by two pathways, decomposition of MeTeTeMe by extrusion of Te and the formation of MeTeMe,[17,18] or by ligand redistribution. We have verified

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[26] The percentage of allyl radicals trapped is calculated from the difference in the percentage of propene observed in entries 4 and 5 in table III to account for similar concentrations of diallyltellurium.

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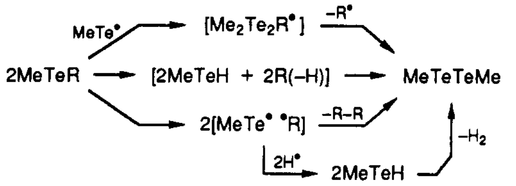
that the sole volatile product of pyrolytic decomposition of dimethylditellurium under similar conditions was MeTeMe. Only small amounts of symmetrical RTeR compounds (<1%) could be detected in the decomposition of MeTeR compounds. If ligand redistribution were a major decomposition pathway, then greater amounts of the RTeR compounds would be expected to survive under the experimental conditions. Ligand redistribution also does not account for the formation of dimethylditellurium, the dominant tellurium-containing product from MeTeR pyrolysis. Therefore, dimethyltellurium most likely arose from the decomposition of dimethylditellurium.

Dimethylditellurium can be formed by the combination of two MeTe• radicals, by dehydrogenative coupling of two MeTeH molecules, or by reactions of MeTeR with MeTe• as illustrated in reaction 4. Methanetellurol, MeTeH, might be formed by H• abstraction by MeTe• or by a β-hydrogen elimination reaction directly from MeTeR. Methanetellurol and methane were not detected in these experiments. Methanetellurol would be unstable in the temperature regime of these experiments and hence undetectable. The failure to observe methane may be the result of low concentrations of MeTeH or decomposition by dehydrogenative coupling. It was previously verified that pyrolysis of MeTeMe does not lead to the observation of MeTeTeMe under these conditions.



(4)

The nature of the organic products derived from the R group in the MeTeR compounds was a function of the structure of R and the radicals formed from Te–R bond homolysis. For both MeTe(allyl) and MeTe(2-methylallyl), the major organic byproducts (>99%) observed were 1,5-hexadiene and 2,5-dimethyl-1,5-hexadiene, respectively. Less than 1% propene and butene, respectively, were detected in the decomposition of these compounds. Products resulting from the coupling of methyl and R groups (e.g., butenes and pentenes) were also not detected.

These results suggested that decomposition of MeTe(allyl) and MeTe(2-methylallyl) proceeded by homolysis of the Te–R bond to generate MeTe• and R• radicals. The fate of some portion of the MeTe• radicals is the formation of MeTeTeMe. The carbon-centered radicals end up as R–R compounds. Attempts to trap the allyl radicals with 1,4-cyclohexadiene (a source of hydrogen atoms) resulted in the observation of 25% propene at 350 °C.

Methylbenzyltellurium decomposed to form bibenzyl as the dominant organic product by GC and GC/MS. Toluene was not detected. When MeTe(benzyl) was pyrolyzed as a 1% solution in 1,4-cyclohexadiene, toluene was detected, demonstrating the presence of benzyl radicals.

The absence of reactive β-hydrogens in MeTeR compounds for R = allyl, 2-methylallyl, and benzyl did not permit a comparison of the relative rates of the β-hydrogen elimination and homolysis pathways. Methyl-*tert*-butyltellurium can serve as an effective model for the β-hydrogen elimination reaction. Pyrolysis of MeTe^{t}Bu at 350 °C led to a mixture of isobutene, isobutane, MeTeMe, and MeTeTeMe. The observed 39:61 ratio of isobutane to isobutene was independent of temperature and different from the 48:52 ratio observed in the decomposition of ^{t}Bu$_2$Te. Butene can be formed from MeTe^{t}Bu by either a β-hydrogen elimination or disproportionation of ^{t}Bu• radicals, while isobutane could arise from H• abstraction by ^{t}Bu• radicals or decomposition of ^{t}BuTeH. The latter pathway to isobutane formation is considerably less favorable, as it requires α-hydrogen elimination from MeTe^{t}Bu or homolysis of the Me–Te bond and H• abstraction by the resulting ^{t}BuTe• radical. There is no precedent for such reactions in the literature, nor does experimental evidence (^{t}BuTeH was not detected) support either pathway.[1-4]

The observed isobutane to isobutene ratio from decomposition of MeTe^{t}Bu is significantly shifted in favor of isobutene when compared with decomposition of ^{t}Bu$_2$Te or ^{t}Bu$_2$N$_2$ under identical conditions. Observation of considerably more isobutene argues in favor of a β-hydrogen elimination pathway. Direct observation of MeTeH, the other product of β-hydrogen elimination, would greatly strengthen this proposed pathway. The difficulties in detecting MeTeH under the experimental conditions and the presence of reaction pathways for MeTeH were noted (vide infra). The observation of methanol in the decomposition of methyl *tert*-butyl ether has been suggested as evidence for a β-hydrogen elimination pathway in the latter compound.[21]

Pyrolysis of a 1% solution of MeTe(^{t}Bu) in 1,4-cyclohexadiene shifted the isobutane to isobutene ratio in favor of isobutane (76:24). Under similar conditions, pyrolysis of a 1% solution of 2,2′-azoisobutane (^{t}BuN=N^{t}Bu) in 1,4-cyclohexadiene yielded an isobutane/isobutene ratio of 91:9, while pyrolysis of 1% di-*tert*-butyltellurium in 1,4-cyclohexadiene yielded a ratio of isobutane to isobutene of 64:36. The shift in the isobutane to isobutene ratio in favor of isobutane during copyrolysis of MeTe^{t}Bu in 1,4-cyclohexadiene suggested that a significant fraction of the pyrolysis proceeded through formation of *tert*-butyl radicals. We believe that the observed decomposition products in the pyrolysis of both MeTe^{t}Bu and (^{t}Bu)$_2$Te are consistent with competitive β-hydrogen elimination and bond homolysis pathways.

In contrast to the MeTeR compounds, the unsymmetrical tellurium compound ^{t}BuTe(allyl) contains two weak Te–C bonds. Decomposition can occur either by homolysis of the Te–C bond or by β-hydrogen elimination to form isobutene and (allyl)TeH. The product distribution in the pyrolytic decomposition of ^{t}BuTeR compounds should be diagnostic of the relative roles of bond homolysis and β-hydrogen elimination pathways.

Pyrolysis of ^{t}BuTe(allyl) showed a significantly different product distribution from that obtained from decomposition of the symmetrical compounds, indicating that ligand redistribution did not dominate the decomposition pathway (Table V, entries 1–3). The ligand redistribution between ^{t}BuTe(allyl),(allyl)$_2$Te, and (^{t}Bu)$_2$Te was found to be much slower (months) than the equilibration of (allyl)$_2$Te, (2-methallyl)$_2$Te, and (allyl)(2-methylallyl)Te (days) at 80 °C in benzene solution.[3] The product of ^{t}Bu• and allyl• radical combination, 4,4-dimethyl-1-pentene, was observed in significant quantities (11%), while the analogous 2,2,3,3-tetramethylbutane was not detected during pyrolysis of (^{t}Bu)$_2$Te.[3] In contrast to the decomposition of diallyltellurium, 10% propene was observed from pyrolysis of ^{t}BuTe(allyl), while less than 2% was observed from pyrolysis of (allyl)$_2$Te. The balance of the product was isobutane, isobutene, and 1,5-hexadiene. The ratios of 1,5-hexadiene to propene and butane to butene were also different from those observed for the symmetrical compounds (Table VI, entries 1–3). The increased amount of propene observed in the decomposition reactions of ^{t}BuTe(allyl) probably arose from the β-hydrogen elimi-

Table V. Products from the Pyrolysis of ^{t}BuTe(allyl),(allyl)$_2$Te, and (^{t}Bu)$_2$Te at 300 °C

	products,[a] %				
	propene	isobutane	isobutene	1,5-hexadiene	4,4-dimethyl-1-pentene
1. ^{t}BuTe(allyl)	9.6	15.9	26.7	36.8	11.0
2. (allyl)$_2$Te	1.8			98.2	
3. (^{t}Bu)$_2$Te		46.2	53.8		
4. 1% ^{t}BuTe(allyl) in benzene	12.3	14.2	31.8	31.2	10.5
5. 1% (allyl)$_2$Te in benzene	1.5			98.5	
6. 1% (^{t}Bu)$_2$Te in benzene		36.7	63.3		
7. 1% ^{t}BuTe(allyl) in cyclohexadiene	17.6	36.1	17.5	23.4	5.3
8. 1% (allyl)$_2$Te in cyclohexadiene	6.7			93.3	
9. 1% (^{t}Bu)$_2$Te in cyclohexadiene		63.8	36.2		

[a] Normalized by the number of carbon atoms.

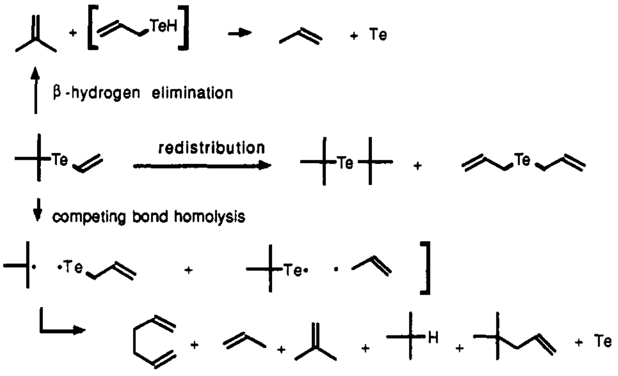
Table VI. Product Ratios from the Pyrolysis of ^{t}BuTe(allyl),(allyl)$_2$Te, and (^{t}Bu)$_2$Te at 300 °C

	ratio[a]	
	1,5-hexadiene/propene	isobutane/isobutene
1. ^{t}BuTe(allyl)	79:21	37:63
2. (allyl)$_2$Te[b]	98:2	
3. (^{t}Bu)$_2$Te[b]		46:54
4. 1% ^{t}BuTe(allyl) in benzene	72:28	31:69
5. 1% (allyl)$_2$Te in benzene	98:2	
6. 1% (^{t}Bu)$_2$Te in benzene		37:63
7. 1% ^{t}BuTe(allyl) in cyclohexadiene	57:43	67:33
8. 1% (allyl)$_2$Te in cyclohexadiene	93:7	
9. 1% (^{t}Bu)$_2$Te in cyclohexadiene		64:36

[a] Normalized by the number of carbon atoms.

nation of isobutene and generation of (allyl)TeH, which subsequently decomposed to propene (Scheme VI). Based on the pyrolysis data for (allyl)$_2$Te, formation of propene and allene from intramolecular (allyl)/(allyl)Te radical chemistry appeared unlikely. Similarly, the reported lack of reactivity of allyl radicals toward H$^{\bullet}$ sources (vide infra)[9,24] favors a β-hydrogen elimination pathway over H$^{\bullet}$ abstraction from ^{t}BuTe(allyl) or ^{t}Bu radicals. The independent synthesis of (allyl)TeH has not been realized, preventing independent verification of its decomposition products.

Scheme VI. Proposed Pathways for the Decomposition of ^{t}BuTe(allyl)



Conclusions

The gas-phase pyrolytic decomposition of symmetrical and unsymmetrical organotellurium compounds occurs primarily by bond homolysis. Compounds with reactive β-hydrogens such as ^{i}Pr$_2$Te, ^{t}Bu$_2$Te, and RTe^{t}Bu (R = Me, allyl) may also decompose by a β-hydrogen elimination pathway to produce alkanetellurols and dialkyl ditellurides. Sufficient stability of alkyltellurium radicals has been demonstrated by the formation of (^{t}Bu)$_2$Te$_2$ and Me$_2$Te$_2$ (k_2 is not greater than k_1 in reaction 1). An unreactive β-hydrogen in diallyl telluride also shuts down the β-hydrogen elimination pathway. Pyrolysis of diallyl telluride and allyl-like tellurium compounds proceeds by a Te–C bond homolysis pathway similar to that observed for azo compounds, albeit with a different rate-determining step. Intramolecular pathways and an ene-type mechanism appeared unlikely to contribute significantly to the decomposition of diallyl telluride. Work is in progress to obtain kinetic data for these processes and information on the implications for the CVD of tellurium containing alloys.

Registry No. *t*-BuTeSiMe$_3$, 135107-03-8; MeOSiMe$_3$, 1825-61-2; *i*-Pr$_2$Te, 51112-72-2; *t*-Bu$_2$Te, 83817-35-0; $CH_2{=}C(CH_3)(CH_2)_2Br$, 20038-12-4; $CH{=}CHCH_2TeCH_2CH{=}CH_2$, 113402-46-3; $CH_2{=}C(CH_3)CH_2TeCH_2C(CH_3){=}CH_2$, 135106-99-9; bis(3-methyl-3-butenyl)telluride, 135107-00-5; methyl(allyl)tellurium, 114438-52-7; methyl(2-methylallyl)tellurium, 135107-01-6; methyl(*tert*-butyl)tellurium, 83817-28-1; methyl(benzyl)tellurium, 103680-41-7; tellurium, 13494-80-9; allyl bromide, 106-95-6; 2-methylallyl chloride, 563-47-3; allyl chloride, 107-05-1; methyl iodide, 74-88-4; benzyl bromide, 100-39-0; *tert*-butyl(allyl)tellurium, 118635-94-2; 3-chloro-1-propene, 107-05-1; 2-methyl-2-propanyltellurol, 135107-02-7; *tert*-butyllithium, 594-19-4; chlorotrimethylsilane, 75-77-4.