Organometallics 1989, *8*, 1674–1678

Synthesis and Characterization of Diallyl Telluride and Allyl Methyl Telluride

Kelvin T. Higa* and Daniel C. Harris

Chemistry Division, Research Department, Naval Weapon Center, China Lake, California 93555

Received November 8, 1988

Diallyl telluride and allyl methyl telluride were prepared and characterized by ^{1}H, ^{13}C, and ^{125}Te NMR, mid- and far-IR, and UV spectroscopy. The reaction of disodium telluride with 2 equiv of allyl bromide in absolute ethanol at 0 °C under an argon atmosphere affords diallyl telluride in 83% yield. Allyl methyl telluride was prepared and isolated in 62 and 58% yields by the reaction of allyl–Te–MgBr with CH_3I and by the reaction of $LiTeCH_3$ with allyl bromide, respectively. Neat diallyl telluride decomposes at 180–183 °C to give a Te film and the coupled product 1,5-hexadiene. In the presence of light, allyl methyl telluride pyrolyzes at 60–80 °C to give a tellurium film and a mixture consisting mainly of 1-butene and 1,5-hexadiene.

Introduction

Diorganyl tellurides compounds are of biological interest[1] and find use in organic synthesis,[2,3] organic superconductors,[4,5] and photographic imaging.[6] The semiconductor mercury cadmium telluride[7-11] can be prepared by the metal–organic chemical vapor deposition (MOCVD) process from diethyl telluride, dimethyl cadmium, and elemental mercury at 390–450 °C. At these high temperatures, the deposited film degrades by evaporation of mercury and diffusion of mercury at the film–substrate interface. To address these problems, low-temperature deposition techniques were developed, which include photoassisted MOCVD,[12] precracking MOCVD,[13] plasma-enhanced chemical vapor deposition,[14] and the use of alternate tellurium source compounds with low cracking temperatures.[7,8] Hoke and co-workers demonstrated that diisopropyl telluride,[7] di-*tert*-butyl telluride,[8] and diallyl telluride[9] allow epitaxial films of HgTe to be deposited at 320, 250, and 180 °C, respectively. This paper describes the efficient synthesis of diallyl telluride and allyl methyl telluride and shows how ultra-high-purity tellurium ingots can be used as a starting material to prepare "electronic grade" diorganyl tellurides.

Experimental Section

All reactions were carried out under an argon atmosphere by using standard Schlenk techniques.[15] Glassware was wrapped with aluminum foil and covered with a black cloth to minimize exposure to light unless otherwise noted. Starting materials and products were loaded into glassware under helium in a Vacuum Atmospheres drybox. Tetrahydrofuran (THF) was distilled from sodium and benzophenone. Absolute ethanol was distilled and degassed by the freeze–thaw process under argon.

^{1}H, ^{13}C, and ^{125}Te NMR spectra were recorded on either an IBM NR-80 or Nicolet 200-WB Fourier transform multinuclear spectrometer. Proton coupling constants were refined by computer simulation. ^{125}Te spectra of 1.0 M samples in C_6D_6 were referenced to an external solution of 1.0 M diethyl telluride in C_6D_6, with a chemical shift taken to be 380 ppm relative to a neat sample of dimethyl telluride at 0 ppm. IR spectra were recorded on a Nicolet 7199 or 60SX spectrophotometer using neat films between KBr plates (mid-IR) or neat liquids in 0.2-mm polyethylene cells (far-IR). UV spectra were recorded on a Cary 17D spectrophotometer using Teflon-capped quartz cells.

Chemicals were obtained from the Aldrich Chemical Co. Allyl bromide (97%) was distilled under argon. A 2.0 M solution of (allyl)MgBr in THF was used as received. Methyl iodide was purified by the following methods: (a) Methyl iodide was shaken with an equal volume of 0.1 M aqueous $Na_2S_2O_3$ until the organic phase became colorless. The organic phase was separated, washed with distilled water, dilute aqueous Na_2CO_3, and distilled water, then dried with $CaCl_2$, and finally distilled under argon.[16] (b) Under an argon atmosphere, methyl iodide was refluxed over sodium until nearly colorless and then distilled. Tellurium powders, 60 mesh (99.999%) and 200 mesh (99.8%), were ground in a glovebox immediately prior to use. Elemental analyses were performed by Galbraith Laboratories, Inc.

Disodium Telluride. Tellurium ingots (99.9995%) were broken into pieces (about 2 × 2 × 10 mm) by shaking in a polyethylene container. A 25-mL Schlenk flask was charged with tellurium ingot pieces (6.1 g, 48 mmol), sodium (2.2 g, 96 mmol), naphthalene (0.1 g, 0.8 mmol), and 20 mL of THF. The reaction mixture was stirred for 4 days at 25 °C and filtered. The solid was washed with 20 mL of fresh THF and dried under vacuum to give 7.6 g (44 mmol, 92%) of Na_2Te. Alternatively, 60-mesh Te powder was treated with 2 equiv of sodium naphthalide. After the mixture was stirred for 8 h, the beige product was filtered, washed with 50 mL of fresh THF, and dried under vacuum. The use of 2 equiv of sodium naphthalide in place of sodium reduced the reaction time to less than 4 h. These reactions were performed under normal laboratory lights.

Diallyl Telluride. Over a 1-h period, allyl bromide (93.2 g, 0.770 mol) was added to a stirred slurry of Na_2Te (62.9 g, 0.362 mol) in 400 mL of absolute ethanol at 0 °C. The reaction mixture was stirred at room temperature for 1 h and filtered. The gray solid was washed with 400 mL of ethanol. The washings and filtrate were combined, and the ethanol was removed by distillation at atmospheric pressure leaving crude diallyl telluride (83% yield) as the residue. The product was distilled at 70–72 °C (13 Torr) to yield 57.3 g (75.4%) of pure diallyl telluride as a pungent, air-sensitive, yellow liquid. Anal. Calcd for $C_6H_{10}Te$: C, 34.36; H, 4.81; Te, 60.84. Found: C, 34.42; H, 5.01; Te, 59.83; 59.84. NMR data are listed in Tables I and II. The ^{125}Te proton-coupled NMR spectrum shows a pentet at δ 397 with $^2J_{TeH}$ = 30 Hz.

---

(1) Goodman, M. M.; Knapp, F. F., Jr. *Organometallics* **1983**, *2*, 1106.

(2) Petragnani, N.; Comasseto, J. V. *Synthesis* **1986**, 1.

(3) Engman, L. *Acc. Chem. Res.* **1985**, *18*, 274.

(4) Williams, J. M.; Beno, M. A.; Wang, H. H.; Leung, P. C.; Emge, T. J.; Geiser, U.; Carlson, K. D. *Acc. Chem. Res.* **1985**, *18*, 261.

(5) Wudl, F. *Acc. Chem. Res.* **1984**, *17*, 227.

(6) Gysling, H. J.; Lelental, M.; Mason, M. G.; Gerenser, L. J. *J. Photogr. Sci.* **1980**, *28*, 209.

(7) Hoke, W. E.; Lemonias, P. J. *Appl. Phys. Lett.* **1985**, *46*, 398.

(8) Hoke, W. E.; Lemonias, P. J. *Appl. Phys. Lett.* **1986**, *48*, 1669.

(9) Korenstein, R.; Hoke, W. E.; Lemonias, P. J.; Higa, K. T.; Harris, D. C. *J. Appl. Phys.* **1987**, *62*, 4929.

(10) Lichtman, L. S.; Parsons, J. D.; Cirlin, E.-H.; Brown, D. W. *J. Appl. Phys.* **1988**, *86*, 217.

(11) Parsons, J. D.; Lichtman, L. S. *J. Appl. Phys.* **1988**, *86*, 222.

(12) (a) Irvine, S. J. C.; Mullin, J. B. *J. Cryst. Growth* **1981**, *55*, 107. (b) Irvine, S. J. C.; Tunnicliffe, J.; Mullin, J. B. *J. Cryst. Growth* **1983**, *65*, 479. (c) Mullin, J. B.; Irvine, S. J. C. *J. Vac. Sci. Technol.* **1982**, *21*, 178.

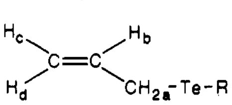
(13) Wang, C.-H.; Lu, P.-Y.; Williams, L. M. Presented at the Seventh American Conference On Crystal Growth/The Third International Conference On II-VI Compounds, Monterey, CA, 1987.

(14) Williams, L. M.; Lu, P.-Y.; Chu, S. N. G. Presented at the Seventh American Converence On Crystal Growth/The Third International Conference On II-VI Compounds, Monterey, CA, 1987.

(15) Shriver, D. F.; Drezdzon, M. A. *The Manipulation of Air Sensitive Compounds*, 2nd ed.; Wiley: New York, 1986.

(16) Perrin, D. D.; Armarego, W. L. F.; Perrin, D. R. *Purification of Laboratory Chemicals*, 2nd ed.; Pergamon Press: Elmsford, NY, 1980; p 335.

Table I. ^1H NMR Data[a] for Diallyl Telluride and Allyl Methyl Telluride



compound	H_a	H_b	H_c	H_d	CH_3
$(CH_2{=}CHCH_2)_2Te$	δ 3.05 $^2J_{TeH} = 29$	δ 5.85 $^3J_{TeH} = 3.7$ $^3J_{H_bH_a} = 7.9$ $^3J_{H_bH_c} = 9.7$ $^3J_{H_bH_d} = 16.9$	δ 4.66 $^4J_{H_cH_a} = 0.7$ $^3J_{H_cH_b} = 9.7$ $^2J_{H_cH_d} = 1.8$	δ 4.68 $^4J_{H_dH_a} = 1.1$ $^3J_{H_dH_b} = 16.9$ $^2J_{H_dH_c} = 1.8$	
$CH_2{=}CHCH_2TeCH_3$	δ 2.96 $^2J_{TeH} = 31$	δ 5.77 $^3J_{TeH} = 3.2$ $^3J_{H_bH_a} = 8.0$ $^3J_{H_bH_c} = 9.75$ $^3J_{H_bH_d} = 16.9$	δ 4.59 $^4J_{H_cH_a} = 0.7$ $^3J_{H_cH_b} = 9.75$ $^2J_{H_cH_d} = 1.65$	δ 4.60 $^4J_{H_dH_a} = 0.9$ $^3J_{H_dH_b} = 16.9$ $^2J_{H_dH_c} = 1.65$	δ 1.55 $^2J_{TeH} = 22$

[a] J values in hertz.

Table II. ^{13}C NMR of Organotellurium Compounds[a]

compounds	Me–Te	C_α or ipso	C_β or ortho	C_γ or meta	C_δ or para
Me_2Te[b]	−21.5 (158)				
Et_2Te[c]		−6.5 (151)	17.9 (12)		
J_{CH}		141	127		
n-Bu_2Te[d]		1.8 (156)	34.7 (11)	25.2 (11)	13.4
t-Bu_2Te[c]		26.6 (186)	36.8 (31)		
J_{CH}			126		
$(allyl)_2Te$[c]		6.3 (146)	137.5	114.6	
J_{CH}		137	152	153	
Ph_2Te[b]		114.7	137.8 (54)	129.2	127.5
PhTeMe[b]	−16.7 (163)	112.5	136.7 (55)	129.0	127.0
t-BuTeMe[c]	−22.2 (181)	21.0 (138)	35.6 (30)		
J_{CH}	140		126		
BuC≡C—TeMe[e]	−14.8	33.8	110.8	21.1	31.8
$CH_2{=}CHC{\equiv}CTeMe$[e]	−14.8	49.5	109.7	117.5	126.8
EtC≡CC≡CTeMe[e]	−14.8	34.6	95.8	65.6	82.6
$\overline{Te(CH_2)_3CH_2}$[b]		5.8 (126)	35.8 (28)		
$\overline{Te(CH_2)_4CH_2}$[b]		−3.6 (131)	28.6 (27)	29	
(allyl)TeMe[c]	−21.0 (170)	5.4 (135)	136.7	114.1	
Me_3SiTe-t-Bu[c]		24.6	39.7 (t-Bu)		
J_{CH}			126		
			4.3 (Me_3Si)		
J_{CH}			121		

[a] The values in parentheses are ^{125}Te–C coupling constants. Chemical shifts in ppm. [b] Hope, E. G.; Kemmitt, T.; Levason, W. *Organometallics* **1988**, *7*, 78. [c] Work done at the Naval Weapons Center at China Lake. [d] Harris, D. C.; Nissan, R. A.; Higa, K. T. *Inorg. Chem.* **1987**, *26*, 765. [e] Kalabin, G. A.; Bzhezovskii, V. M.; Kushnarev, D. F.; Prooidakov, A. G. *Zh. Org. Khim.* **1981**, *17*, 1143.

Allyl Methyl Telluride. A 50-mL Schlenk flask equipped with a magnetic stirring bar and septum was charged with freshly ground Te powder (2.09 g, 16.4 mmol) and 15 mL of THF. Allylmagnesium bromide (8.20 mL, 2.0 M in THF, 16.4 mmol) was added slowly via syringe to the stirred Te slurry at −10 °C over a period of 10 min. After being stirred for an additional 20 min, the reaction mixture was warmed to 0 °C and CH_3I (1.02 mL, 16.4 mmol) was added via syringe. The greenish yellow mixture was stirred for 30 min and filtered, the THF removed at reduced pressure at 35 °C, and the product (3.01 g, 10.2 mmol, 62%) purified by vacuum distillation at 48 °C (19 Torr). Anal. Calcd for C_4H_8Te: C, 26.15; H, 4.39; Te, 69.46. Found: C, 26.39; H, 4.51; Te, 69.52. NMR data are listed in Tables I and II. $^{125}Te\{^1H\}$ NMR spectrum (C_6D_6): δ 188 ppm.

Pyrolysis. Diallyl telluride or allyl methyl telluride (0.2 g) was heated in an evacuated 25-mL flask equipped with a Teflon valve. The flask was immersed in liquid nitrogen, 1 mL of C_6D_6 was condensed into the flask, and the benzene-soluble products were characterized by NMR.

Results and Discussion

In order to prepare pure tellurium compounds for semiconductor film deposition, synthetic methods must utilize high-purity tellurium ingots as starting materials. Diorganyl tellurides are commonly prepared from the reaction of disodium telluride and alkyl halides.[17–19] Disodium telluride can be prepared by the reduction of Te powder with an aqueous solution of "super-hydride", ($LiBEt_3H$),[20] or $NaBH_4$[21] or from the reduction of tellurium with sodium in liquid ammonia.[18] Although the borohydride reagents allow simple preparation of disodium telluride, they are sources of boron contamination that would dope and degrade semiconducting films prepared by using these reagents. The reduction of Te in liquid ammonia is not convenient because of the cooling requirements and the hazards and difficulty involved in working with ammonia.

Here we report the convenient synthesis of disodium telluride from tellurium metal and 2 equiv of sodium naphthalide. Either tellurium powder or tellurium ingots can be used, but the reaction time is much longer for the ingots. Disodium telluride can also be prepared from a mixture of tellurium, sodium, and catalytic amounts of

---

(17) Brandsma, L.; Wijers, H. E. *Recl. Trav. Chim. Pays-Bas* **1963**, *82*, 68.

(18) Irgolic, K. J. *The Organic Chemistry of Tellurium*; Gordon and Breach Science: New York, 1974; p 107.

(19) Shenai-Khatkhate, D. V.; Orrell, E. D.; Mullin, J. B.; Copertino, D. C.; Cole-Hamilton, O. J. *J. Cryst. Growth* **1986**, *77*, 27.

(20) Clive, D. L. J.; Anderson, P. C.; Moss, N.; Singh, A. *J. Org. Chem.* **1982**, *47*, 1641.

(21) Engman, L.; Cava, M. P. *J. Org. Chem.* **1981**, *46*, 4194.

naphthalene. Diallyl telluride was prepared from disodium telluride and allyl bromide in high yield.

Unsymmetrical diorganyl tellurides, R'TeR, can be prepared from LiTeR[22] or R–Te–Mg–X[23] and an alkyl halide, R'X. The preparation of LiTeR and R–Te–Mg–X is straightforward when using freshly ground tellurium powder. The use of tellurium ingots in the preparation of LiTeR or R–Te–Mg–X is complicated by a redistribution reaction (eq 1) which leads to the formation of Li_2Te or $Te(MgX)_2$. The subsequent addition of an alkyl halide,

$$2RTeM \rightleftharpoons R_2Te + M_2Te \qquad (1)$$

$$M = Li, MgBr$$

R'X, leads to the isolation of the symmetrical products R_2Te and R'_2Te and the unsymmetrical product R–Te–R'. The redistribution reaction can be reduced by using THF instead of diethyl ether as the solvent and reducing the reaction temperature. In the preparation of allyl methyl telluride via either the lithium or Grignard reagent, use of THF as a solvent at −10 °C resulted in a 9:1 molar ratio of diallyl telluride and allyl methyl telluride. The use of diethyl ether as a solvent resulted in a 1:9 ratio under identical conditions. Precipitation of Li_2Te and $Te(MgX)_2$ from the ether solution drive the equilibrium to the right in eq 1, giving higher yields of the symmetrical products.

Isolating high yields of allyl methyl telluride is also hampered by codistillation of the product with THF and by a redistribution reaction (eq 2) which leads to the formation of dimethyl telluride and diallyl telluride. A

$$2R\text{–}Te\text{–}R' \rightleftharpoons R_2Te + R'_2Te \qquad (2)$$

0.1 M benzene solution of allyl methyl telluride heated to 60 °C for 10 min in the dark results in a 1:1:1 molar ratio of dimethyl telluride, diallyl telluride, and allyl methyl telluride. The redistribution occurs more slowly at lower temperatures, but the initiation temperature has not been determined.

Diallyl telluride decomposes at about 180 °C in the light or in the dark to give a tellurium film and 1,5-hexadiene. At ambient temperature, diallyl telluride decomposes in the light over a period of several days but is stable in the dark. Clive and co-workers[20] reported the coupling of allylic groups in the presence of disodium telluride at less than 110 °C via diallylic telluride intermediates. In all cases, the diallylic tellurides were less stable than diallyl telluride. The lower stability they observed was presumably due to the lower stability of cyclic diallylic tellurides, the decomposition of the intermediates in the light, and the fact that they were decomposing mixtures rather than pure compounds. Allyl methyl telluride decomposes in the light at 60–80 °C to give a tellurium film and a 2:1 mixture of 1-butene and 1,5-hexadiene and smaller amounts of dimethyl telluride, diallyl telluride, dimethyl ditelluride, and other unidentified products. No tellurium film is deposited at 80 °C in the dark. Although diallyl telluride and allyl methyl telluride are photosensitive, the enhanced sensitivity of allyl methyl telluride makes it a good candidate for the photoassisted and laser-assisted MOCVD of mercury cadmium telluride. Recently, allyl methyl telluride has been utilized in the photoassisted metal–organic chemical vapor deposition of HgTe and CdTe.[11]

NMR Spectra. The ^1H NMR spectral data for diallyl telluride and allyl methyl telluride are presented in Table I. The allyl group exhibits resonances in the range δ 6.1–5.5 ppm for the methine proton, H^b, δ 4.8–4.4 ppm for the methylene protons, H^c and H^d, and δ 3.1–2.8 ppm for the methylene protons, H^a ($^2J_{TeH}$ = 29–31 Hz), and a chemical shift of δ 1.55 ppm for the methyl group ($^2J_{TeH}$ = 22 Hz) in allyl methyl telluride.

^{13}C NMR data for several diorganyltellurides are listed in Table II. The spectra of the allyl groups in diallyl telluride and allyl methyl telluride are nearly identical and they are similar to those of allyl iodide, for which we observe the α-, β-, and γ-carbons at δ 5, 136, and 117 ppm, respectively. The chemical shift for the methyl group in allyl methyl telluride (δ −21 ppm) is also similar to those of $(CH_3)_2Te$ and CH_3I (δ −21.5 and −22 ppm, respectively).

^{125}Te NMR is the most useful technique for the identification of the components of a tellurium mixture. The chemical shifts are found in a wide range of 0 to more than 1000 ppm for organyl tellurides and ditellurides. O'Brien et al. have demonstrated that the chemical shifts for dialkyl telluride[24] and dialkyl ditelluride[25] compounds can be predicted. Substitution at the α-, β-, and γ-carbon leads to additive changes in the chemical shifts. When a proton is replaced by a methyl group on the carbon adjacent to Te, the change in chemical shift is δ 162 ± 5 ppm. Thus, the sequential methyl substitution in the series $(CH_3CH_2)_2Te$, $[(CH_3)_2CH]_2Te$, and $[(CH_3)_3C]_2Te$ gives calculated Te shift values of δ 700 ± 10 ppm (376 + 2 × 162) and 1024 ± 20 ppm (376 + 4 × 162) vs actual values of 696 and 999 ppm, respectively. This additivity can be extended to the chemical shifts of organyl tellurides containing olefinic substituents. The change in chemical shift for methyl to allyl is 208 ± 10 ppm.[26]

Infrared Spectra. We observe that the infrared spectra of alkyl tellurides are very similar to those of the corresponding alkyl iodides. (The same is true of the NMR and ultraviolet spectra.) Table III compares the infrared spectra of diallyl telluride, allyl methyl telluride, allyl iodide, and methyl iodide. For additional comparison, the previously assigned spectra of Me_2Te_2 and Me_2Te are listed. Te–C stretching is generally observed near 500 cm^{-1}. For diallyl telluride we expect one asymmetric and one symmetric stretch, so the two bands at 500 and 480 cm^{-1}, respectively, are logically assigned to these vibrations. Allyl methyl telluride also has two bands in this region, each corresponding closely to the C–I stretching mode of methyl iodide and allyl iodide. The bands near 235 cm^{-1} in diallyl telluride and allyl methyl telluride are assigned as C–Te–C bending modes, by analogy with C–Te–C bending at 198 cm^{-1} in Me_2Te.

UV Spectra. Figure 1 shows the UV spectra of gaseous diallyl telluride, allyl methyl telluride, and for comparison dibutyl telluride.[8] To interpret the spectra of the allyl tellurides, the spectra of simple dialkyl telluride and allyl compounds must be understood. The spectrum of dibutyl telluride is very similar to those of dimethyl telluride[28] and diethyl telluride,[29] so the interpretation of all three is the same.

A schematic diagram of the highest occupied and lowest unoccupied molecular orbitals of dimethyl telluride is given

---

[22] Seebach, D.; Beck, A. K. *Chem. Ber.* **1975**, *108*, 314.

[23] Petragnani, N.; Campos, D. M. *Chem. Ber.* **1963**, *96*, 249.

[24] O'Brien, D. H.; Dereu, N.; Huang, C.-K.; Irgolic, K. J. *Organometallics* **1983**, *2*, 305.

[25] O'Brien, D. H.; Dereu, N.; Grigsby, R. A.; Irgolic, K. J. *Organometallics* **1982**, *1*, 513.

[26] Gedridge, R. W.; Higa, K. T.; Nissan, R. A., manuscript in preparation. The calculated vs observed chemical shifts for the series (allyl)TeR (where R = methyl, ethyl, isopropyl, *tert*-butyl, allyl) are 208 ± 10 (188), 397 ± 12 (387), 559 ± 17 (556), 719 ± 21 (723), and 416 ± 20 (397) ppm, respectively.

[27] Harris, D. C.; Nissan, R. A.; Higa, K. T. *Inorg. Chem.* **1987**, *26*, 765.

[28] Fantoni, R.; Stuke, M. *Appl. Phys. B* **1985**, *38*, 209.

[29] Connors, J.; Greig, G.; Strausz, O. P. *J. Am. Chem. Soc.* **1969**, *91*, 5695.

Table III. Infrared Spectra of Diallyl Telluride ((DA)Te) and Allyl Methyl Telluride ((AM)Te)[a]

(DA)Te	(AM)Te	allyl-I[b]	MeI[b,c]	MeTeTeMe[d]	MeTeMe[e]	
3080 m	3078 s	3084 m				ν(C—H)
3059 w	3060 m					
3030 w	3030 m	3046 w	3045 w			
3001 w	3001 m	3007 w		3007 mw	3001 m	
2975 m	2973 m	2960 w				
2925 m	2922 s	2925 w	2949 m	2920 vs	2921 s	
	2847 w	2862 vw	2835 w		2808 m	
	2808 w		2810 w	2795 mw		
			2466 w	2397 mw	2423 w	
		1847 vw				
1811 w	1809 w			1712 w		
1626 vs	1625 s	1630 m				ν(C=C)
1427 m	1427 s	1440 m	1426 m	1405 s	1417 m	δ_{as}(CH_3 and CH_2)
1397 m	1397 m	1403 m				δ(C—H)(vinyl)
1293 w	1292 w	1290 vw				δ(C—H)(vinyl)
	1219 s		1239 s	1206 vvs	1211 s	δ_s(CH_3)
1191 m	1190 s	1187 m				
1126 s	1129 s	1151 vs				
1041 w	1042 m	1048 w				
				1010 w		2ν(Te—C)
985 vs	984 s	983 s				δ(C—H)(vinyl)
955 w						
903 vs	899 vs	921 vs				δ(C—H)(vinyl)
			884 m		876 m	CH_3 rock
	848 s			824 vs	839 m	CH_3 rock
817 m		825 w				
785 w	774 w					
675 s	675 s	669 vs				
				555 w		3ν(Te—Te)
	525 m		523 m[f]	507 ms	527 m	ν(Te—C)(CH_3)
500 w						ν_{as}(C—Te—C)
	489 m	489 w[f]				ν(Te—C)(allyl)
480 w						ν_s(C—Te—C)
				470 w		
391 w	385 m					
380 vw				380 w		2ν(Te—Te)
239 vw	233 vw				198	δ(C—Te—C)
				189 mw		ν(Te—Te)
	184 vw					
				170 sh		δ(Te—Te—C)

[a] Hydrocarbon assignments from: Bellamy, L. J. *The Infrared Spectra of Complex Molecules*; Wiley: New York, 1958. [b] Data from Nicolet/Aldrich Library Vol. 1 (4000–400 cm^{-1}). Me–I has no absorptions between 400 and 100 cm^{-1}. [c] Methyl iodide assignments from: Herezberg, G. *Infrared and Raman Spectra of Polyatomic Molecules*; Van Nostrand-Reinhold: New York, 1945. [d] Assignments from: Sink, C. W.; Harvey, A. B. *J. Mol. Struct.* **1969**, *4*, 203–214. [e] Present work; see also Freeman, J. M.; Henshall, T. *J. Mol. Struct.* **1967–1968**, *1*, 31–37. [f] ν(I–C).

in Figure 2. Only the TeC_2 framework is considered. The labeling of orbitals follows that of Cradock and Whiteford,[30] who reported the ionization energies based on photoelectron spectroscopy. The order of the Te–C σ-bonding orbitals ($2b_2$ and $3a_1$) is tentative, and the order of the Te–C antibonding σ orbitals ($3b_2$ and $4a_1$) is not known. The highest occupied orbital is the nonbonding $5p_x$(Te).

The lowest lying transitions should be n → σ^* ($1b_1 \rightarrow 3b_2$ and $1b_1 \rightarrow 4a_1$), and we could assign these to the two weak bands of dibutyl telluride whose maxima in pentane solution are observed at 356 nm ($\epsilon = 10^{2.0}$ M^{-1} cm^{-1}) and 288 nm ($\epsilon = 10^{2.2}$ M^{-1} cm^{-1}). According to orbital selection rules for C_{2v} symmetry, the $1b_1 \rightarrow 3b_2$ transition is forbidden, but the $1b_1 \rightarrow 4a_1$ is allowed. The forbidden transition is expected to have an absorptivity in the range of 10^0–10^3 M^{-1} cm^{-1}, while the allowed transition should be more intense (>10^3 M^{-1} cm^{-1}) than we observe. Therefore, an alternative assignment of the bands at 356 and 288 nm is that they are triplet and singlet components of $1b_1 \rightarrow 3b_2$, with the triplet excited state allowed by spin–orbit coupling to the heavy tellurium atom. Either set of assignments attributes antibonding Te–C character

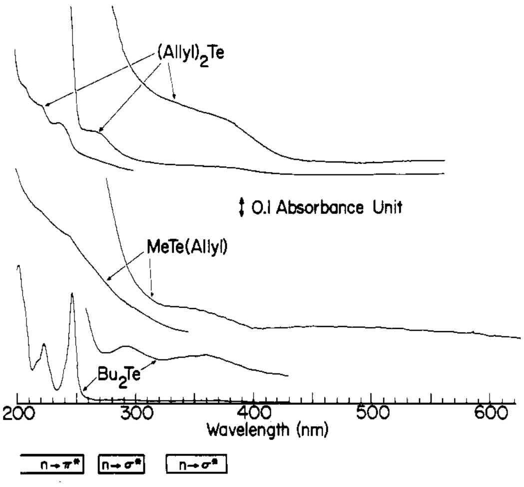


Figure 1. Ultraviolet spectra of gas-phase samples saturated with vapor at approximately 30 °C. For dibutyl telluride, the path length is 10 cm and the upper trace is a 10× sensitivity increase. That is the vertical distance labeled 0.1 absorbance unit is 0.01 for the upper trace. For allyl methyl telluride, the path length is 0.5 cm for the upper trace and 0.1 mm (with a 2× sensitivity increase) for the lower trace. For diallyl telluride, the upper traces were made with a 10-cm cell (with a 5× sensitivity increase for the upper trace). The lower trace for the diallyl telluride was with a 0.5-cm cell.

---

[30] Cradock, S.; Whiteford, R. A. *J. Chem. Soc. Faraday Trans. 2* **1972**, *68*, 281.

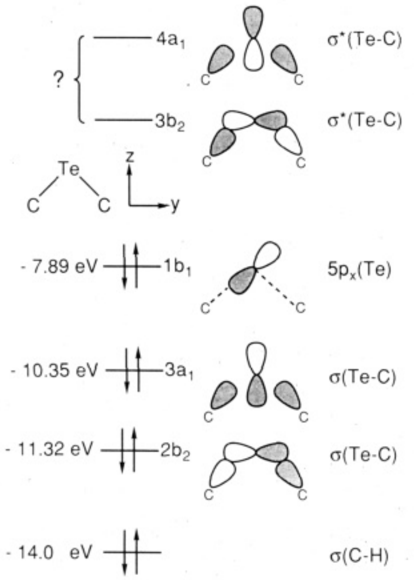


Figure 2. Schematic molecular orbital diagram of TeC_2 fragment of dialkyl tellurides. The molecule is in the *yz* plane, with the C_2 axis parallel to *z*. Ionization energies are from photoelectron spectroscopy of dimethyl telluride.[30]

to the excited states of the 356 and 288 nm transition. Both absorptions should promote Te–C bond breaking.

The three strong bands of dibutyl telluride near 250, 220, and 200 nm (in Figure 1) are assigned to Rydberg transitions in dimethyl telluride.[31] The series $5p_x$(Te) → 6s(Te), $5p_x$ → 7s, $5p_x$ → 8s, etc. begins at 258 nm in dimethyl telluride, and successive transitions are observed at 195, 176, and 168 nm. Strong absorptions at 250 and 243 nm in dimethyl telluride are unassigned but could possibly be the n → σ* ($1b_1 \rightarrow 4a_1$) allowed transition. The Rydberg series $5p_x$(Te) → 6p(Te), $5p_x$ → 7p, $5p_x$ → 8p begins at 220 nm. The Rydberg series $5p_x$(Te) → 5d(Te), $5p_x$ → 6d, $5p_x$ → 7d begins at 201 nm.

In the allyl tellurides, the olefin should lead to an observable UV transition. Allyl iodide has its n(5p(I)) → σ*(I–C) transition at 267 nm ($\epsilon = 10^{2.7}$ M^{-1} cm^{-1}) and n(5p(I)) → π*(C–C) is assigned to a shoulder near 217 nm ($\epsilon = 10^{3.5}$ M^{-1} cm^{-1}).[32] Comparing the spectra of diallyl telluride and allyl methyl telluride to that of dibutyl telluride in Figure 1, it appears that each band of dibutyl telluride has a corresponding band in the other two spectra. The assignments for diallyl telluride are therefore n → σ* at ~360 (shoulder) and ~270 nm and Rydberg series commencing near 236, 223, and below 200 nm. For allyl methyl telluride one n → σ* band is seen near 350 nm. The broadly rising feature between 300 and 200 nm in the spectra of both allyl compounds probably contains the n($5p_x$(Te)) → π*(allyl) absorption.

Acknowledgment. This work was supported in part by the Office of Naval Research and by a postdoctoral fellowship provided by the American Society for Engineering Education. We thank Drs. R. A. Nissan and M. P. Nadler for their assistance with ^{125}Te NMR and infrared spectra.

Registry No. Tellurium, 13494-80-9; disodium telluride, 12034-41-2; allyl bromide, 106-95-6; diallyl telluride, 113402-46-3; allylmagnesium bromide, 1730-25-2; allyl methyl telluride, 114438-52-7; 1,5-hexadiene, 592-42-7; 1-butene, 106-98-9; dimethyl telluride, 593-80-6; dimethyl ditelluride, 20334-43-4.

---

(31) Scott, J. D.; Causley, G. C.; Russell, B. R. *J. Chem. Phys.* **1973**, *59*, 6577.

(32) Boschi, R. A.; Salahub, D. R. *Mol. Phys.* **1972**, *24*, 735.