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The Acetolysis of 2-Acetoxyalkyltellurium Trihalides

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ABSTRACT

The reaction of six 2-acetoxyalkyltellurium trihalides in refluxing dry acetic acid yields haloacetates in addition to the previously observed diacetates. The haloacetates are formed either through direct cleavage of the carbon–tellurium bond with retention of configuration or through initial formation of a neighboring group intermediate that is subsequently attacked by halide ion. Added lithium acetate leads to an increase in S_N2 attack on the tellurium carbon. © 1998 John Wiley & Sons, Inc. Heteroatom Chem **9**:85–93, 1998

INTRODUCTION

Tellurium(IV) oxide, solubilized by reaction with lithium halides in acetic acid (Equation 1, X = Cl, or Br), has been used extensively in the oxidation of alkenes to *vic*-diacetates [1,2], for the oxidation of aromatic and carbonyl compounds [3] and for selective diacetoxylation of conjugated [4] and nonconjugated [5] dienes. It has been shown previously that the oxidation of alkenes is a two-step process. In the first step of the oxidation, a tellurium(IV) species such as **1** electrophilically attacks the carbon–carbon π bond to form 2-acetoxyalkyltellurium

$$TeO_2 + LiX \xrightarrow{HOAc} Te(OAc)_mX_{4-m} \quad (1)$$

compounds (Equation 2a). The stereochemistry of this first step is cleanly antistereospecific. Only bis(*trans*-2-acetoxycycloalkyl) ditellurides are isolated when cyclopentene and cyclohexene are refluxed in acetic acid with a mixture of tellurium tetrachloride and lithium acetate and the intermediate tellurium compound subsequently reduced with sodium thiosulfate [6]. Similarly, *cis*-2-butene forms only bis(*threo*-2-acetoxybutyl) ditelluride, and *trans*-2-butene forms only bis(*erythro*-2-acetoxybutyl) ditelluride.

In the second step of the oxidation, the carbon–tellurium bond is cleaved to yield *vic*-diacetates (Equation 2b). The acetolysis of *trans*-2-acetoxyalkyltellurium tribromides, studied to model the second step in the oxidation reaction, showed that the stereochemistry of the diacetate depended upon the structure of the tribromide [6]. The loss of stereoselectivity in the acetolysis of the tribromide, the second step in the oxidation reaction, was explained as a competition between rearward attack by acetate ion at the tellurium carbon and neighboring acetoxy participation.

$$R-CH=CH-R \xrightarrow[LiOAc]{TeCl_4,HOAc}$$

$$\begin{array}{c} R-CH-CH-R \\ \quad | \qquad | \\ AcO \qquad Te(AOc)_mCl_{3-m} \end{array} \quad (2a)$$

Dedicated to Prof. William E. McEwen on the occasion of his seventy-fifth birthday.

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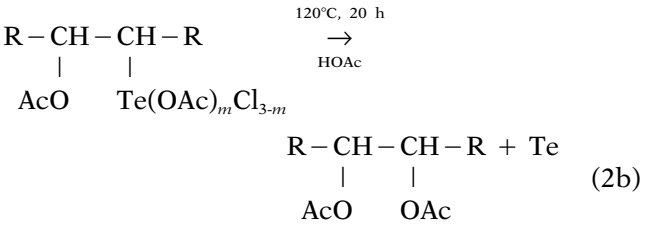


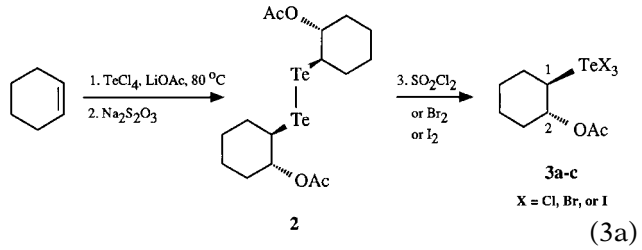
$$\begin{array}{l} R-CH-CH-R \\ \quad\;| \quad\;| \\ AcO \quad Te(OAc)_m Cl_{3-m} \end{array} \xrightarrow[HOAc]{120°C,\ 20\ h} \begin{array}{l} R-CH-CH-R \\ \quad\;| \quad\;| \\ AcO \quad OAc \end{array} + Te \qquad (2b)$$

However, the acetolysis reactions were carried out for long periods at high temperatures (120°C), excess lithium acetate was usually present, and the water content of the acetic acid was not rigorously controlled. We have now conducted a more detailed study of this acetolysis reaction with three *trans*-2-acetoxycyclohexyltellurium trihalides and three 2-acetoxyheptyltellurium trihalides and have found the reaction to be somewhat more complicated than originally reported.

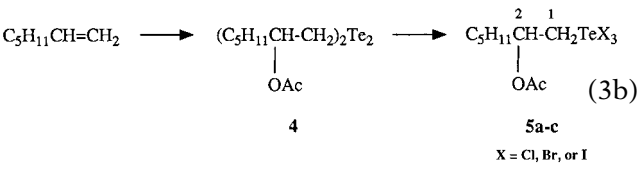
RESULTS AND DISCUSSION

Syntheses and Characterization of 2-Acetoxyalkyltellurium Trihalides

Six 2-acetoxyalkyltellurium trihalides, **3a–c** and **5a–c,** were prepared and characterized by NMR spectroscopy. Cyclohexene was reacted with a homogeneous solution of tellurium tetrachloride and lithium acetate in acetic acid at a temperature of 80°C for 3 hours (Equation 3a). After this period, the mixture was reduced with aqueous sodium thiosulfate to give bis(*trans*-2-acetoxycyclohexyl) ditelluride **2.** Treatment of the solution containing the ditelluride with sulfuryl chloride, bromine, or iodine gave the *trans* trihalides **3a–c.** In a similar manner, trihalides **5a–c** were prepared from 1-heptene with ditelluride **4** as intermediate (Equation 3b).



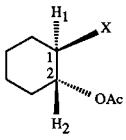
(3a)



(3b)

The chemical shifts for carbons **1** and **2** and their protons are presented in Tables 1 and 2. The hydrogens on tellurium-bearing carbon **1** appear between 3.92 and 4.48 δ, whereas the hydrogens on acetoxy-bearing carbon 2 appear between 5.15 and 5.63 δ. The coupling constant between H-1 and H-2 was approximately 10 Hz for compounds **3a–c,** indicating that the stereochemistry is *trans*. The hydrogens on carbon **1** for compounds **5a–c** are diastereotopic and therefore appear as separate resonances. The carbon-13 shifts for carbon **1** appear between 76.6 and 52.4 δ. This upfield trend reflects the decrease in the electron-withdrawing influence of the halogens on tellurium in going from chlorine to bromine to iodine.

TABLE 1 ^{1}H and ^{13}C Chemical Shifts for **3a–c** and Acetolysis Products **6a–c, 7,** and **8**

Compound					
	X	H_1	C_1	H_2	C_2
3a	$TeCl_3$	4.22	76.6	5.15	77.8
6a[a]	Cl	3.77	60.7	4.74	75.8
3b	$TeBr_3$	4.40	71.6	5.18	77.6
6b[a]	Br	3.90	52.9	4.82	75.8
3c	TeI_3	4.30	60.4	5.22	76.6
6c[a]	I	4.00	37.8	4.83	76.7
7	OAc (*cis*)			4.96	70.9
8	OAc (*trans*)			4.73	73.6

[a]Compounds **6a–c** were synthesized separately and gave the same chemical shifts (see Experimental).

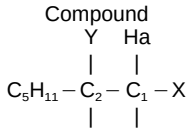
Acetolysis of 2-Acetoxyalkyltellurium Trihalides

The 2-acetoxyalkyltellurium trihalides **3a–c** and **5a–c** were dissolved in *dry* acetic acid to give homogeneous solutions. After 20 hours of reflux, the product mixture contained appreciable amounts of haloacetates **6, 9,** and **10** in addition to the previously observed diacetates [Equation 4, Table 3 (entries 1, 2, and 3), and Table 4]. In these reactions, the acetic acid was carefully dried by distillation from acetic anhydride, and lithium acetate was not present.

In the two-step oxidation of alkenes with tellurium(IV) compounds, lithium salts have been routinely used to solubilize the tellurium compound. When this two-step oxidation was conducted with cyclohexene and 1-heptene with tellurium tetrachloride in the absence of lithium acetate and in dry acetic acid, haloacetates **6a, 9a,** and **10a** were again observed (entry 4 of Table 3 and entry 4 of Table 4). The product distributions were very similar to the distributions for the acetolysis of trichlorides **3a** and **5a** in dry acetic acid.

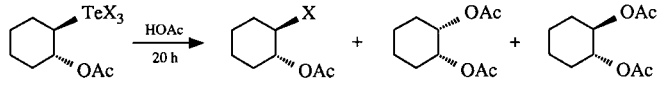
TABLE 2 ^{1}H and ^{13}C Chemical Shifts for **5a–c** and Acetolysis Products **9a–c, 10a–c,** and **11**

Compound

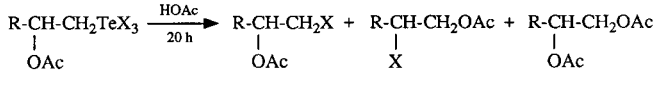


	X	Y	H_a	H_b	C_1	H_2	C_2
5a	$TeCl_3$	OAc	3.92	4.03	66.9	5.45	76.0
9a	Cl	OAc	3.52	3.59	45.6	4.99	72.8
10a	OAc	Cl	4.16	4.20	67.6	4.00	59.2
5b	$TeBr_3$	OAc	4.22	4.33	62.6	5.54	76.3
9b	Br	OAc	3.43	3.34	*b*	*a*	*b*
10b	OAc	Br	*a*	*a*	*b*	*a*	51.7
5c	TeI_3	OAc	4.38	4.48	52.6	5.63	76.8
9c	I	OAc	3.18	3.29	*b*	4.63	*b*
10c	OAc	I	*a*	*a*	*b*	*a*	36.3
11	OAc	OAc	3.91	4.12	65.1	4.96	71.6

[a]Not observed due to overlap with other product resonances:
[b]Not determined.



(4a)



(4b)

The previous oxidations of alkenes with Te(IV) compounds [1,2] and the acetolysis of 2-acetoxyalkyltellurium tribromides [6] had been carried out in glacial acetic acid that had not been carefully dried. When the acetolysis reactions of 2-acetoxycyclohexyltellurium trihalides **3a** and **3b** were carried out in the absence of lithium acetate but in acetic acid that contained a small amount of water, the product distributions changed (entries 5 and 6, Table 3). For **3a,** the amount of chloroacetate diminished, and for tribromide **3b,** no bromoacetate was observed. The product distribution for **3b** in the presence of small amounts of water was similar to that observed previously when the acetolysis of tribromide **3b** was used to model the second step of the oxidation (entry 7) [6]. These results show that acetate ion and small amounts of water substantially alter the product distribution in the second step of the oxidation.

The Formation of the Haloacetates

A proposed reaction sequence for the acetolysis of 2-acetoxycyclohexyltellurium trihalides that includes the formation of the haloacetates is presented as Scheme 1. Winstein and Buckles have shown that solvolysis of *trans*-2-acetoxy-1-halocyclohexanes occurs through the formation of a neighboring group bridged intermediate **12** [7]. This intermediate forms through the rearward attack of the neighboring acetoxy group to give the intermediate with *cis* stereochemistry. The neighboring group intermediate is attacked by charged nucleophiles preferentially at either carbons **1** or **2** resulting in the *trans* diacetate **8** with overall *retention* of configuration. With neutral nucleophiles such as water and acetic acid, competitive attack at carbon **3** occurs [8,9]. Breaking of a carbon **3**–oxygen bond does not result in a change in stereochemistry and overall *inversion* of configuration results. Reaction of the neighboring group intermediate at carbon-**3** gives the monoacetate of the *cis* glycol that is acylated to the *cis* diacetate **7** under the reaction conditions.

The haloacetates are formed early in the reaction either through the direct α-cleavage of the carbon–tellurium bond (pathway **A**) or through initial formation of the neighboring group intermediate **12** followed by reaction with halide ion (pathway **B–C**). After the initial formation of the haloacetates, longer reaction time then leads to the slower solvolysis of the first-formed haloacetates through the neighboring group intermediate to the observed mixture of diacetates.

We are unable to distinguish at this point of the discussion whether either of these two pathways, **A** or **B–C,** is more important in the formation of the haloacetates. The formation of only *trans* haloacetates is consistent with both pathways. α-Cleavage reactions of carbon–tellurium bonds with retention of configuration have been observed in the reactions alkyltellurium trihalides [10]. Formation of the neighboring group intermediate followed by attack by halide ion also results in net retention of configuration.

If pathway **A** is more rapid in the formation of the haloacetates, however, the amount of haloacetate compared to diacetates should be greater earlier in the reaction. If pathway **B–C** is more important, formation of the haloacetates would be competitive with diacetate formation. The ratio of haloacetate to diacetate should remain constant until the reaction of the starting trihalide is complete and the slower solvolysis of the haloacetate takes over. Table 5 presents product distributions for the acetolysis of trihalides **3a–c** at different times. For trichloride **3a,**

TABLE 3 Acetolysis of 2-Acetoxycyclohexyltellurium Trihalides **3a–c**[a]

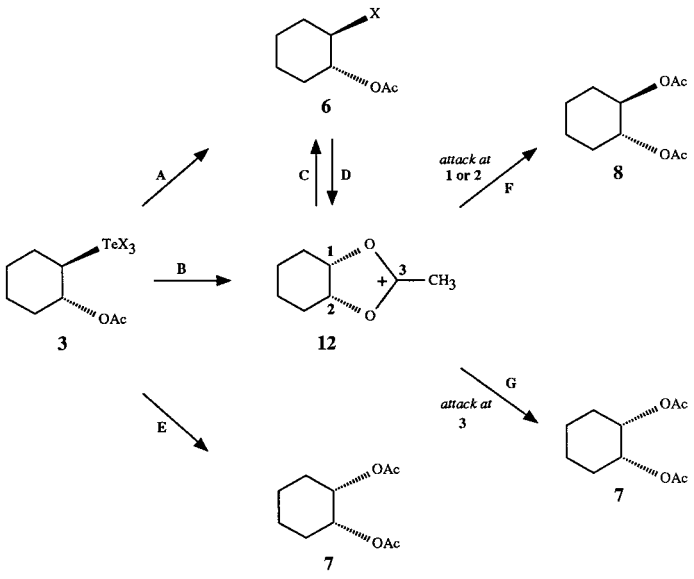
Entry	*Compound*	*Solvent*	*% Yield*	*%**6a–c***	*%**7***	*%**8***
1	**3a**	dry	95.3	76.5	17.2	6.3
2	**3b**	dry	77.9	12.6	52.4	35.0
3	**3c**	dry	79.4	36.6	63.4	0
4	cyclohexene	dry	100.0	79.5	15.3	5.2
5	**3a**	wet	87.2	43.7	52.9	3.4
6	**3b**	wet	71.2	0	87.0	13.0
7	**3b**[b]	wet	76.0	0	77.0	23.0

[a]Reaction conditions: For trihalides **3a–c** (1 mmol), dry HOAc (10 mL) refluxed for 20 h. For cyclohexene (11 mmol), $TeCl_4$ (5 mmol), dry HOAc (20 mL) refluxed for 20 h. Dry HOAc distilled from HOAc-acetic anhydride mixture between 117.6 and 118.2°C. Wet HOAc distilled between 116 and 118°C with no added acetic anhydride.
[b]Ref. [5].

TABLE 4 Acetolysis of 2-Acetoxyheptyltellurium Trihalides **5a–c** ($R = C_5H_{11}$)[a]

Entry	*Compound*	*Solvent*	*% Yield*	R-CHCH$_2$X | OAc *%**9a–c***	R-CHCH$_2$OAc | X *%**10a–c***	R-CHCH$_2$OAc | OAc *%**11***
1	**5a**	dry	83.9	49.6	36.6	13.8
2	**5b**	dry	98.3	13.0	2.4	84.6
3	**5c**	dry	69.6	31.5	13.6	54.9
4	1-heptene	dry		47.3	42.0	10.7

[a]Reaction conditions: For trihalides **5a–c** (1 mmol), dry HOAc (10 mL) refluxed for 20 h. For 1-heptene (11 mmol) $TeCl_4$ (5 mmol), dry HOAc (20 mL) refluxed for 20 h. Dry HOAc distilled from HOAc-acetic anhydride mixture between 117.6 and 118.2°C.

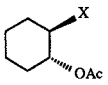
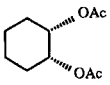
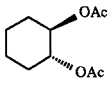


SCHEME 1

little change is observed in the proportion of haloacetate to diacetates for product distributions between 5 and 40 hours indicating pathway **B–C.** For tribromide **3b,** a definite decrease in the amount of haloacetate occurs between 15 minutes and 20 hours. However, product yields qualitatively indicate that the reaction of the tribromide is over after approximately 3 hours so that the later part of this trend merely indicates the progress of the solvolysis of the haloacetate through the neighboring group intermediate.

Product distributions for the acetolysis of 2-acetoxyheptyltellurium tribromide **5b** at different times are presented in Table 6. Solvolysis of the primary alkyltellurium tribromide **5b** is more rapid than solvolysis of cyclohexyltellurium trihalides and product distributions could not be obtained early enough in the reaction to distinguish between direct formation of the bromoacetates or formation through the neighboring group intermediate. However, the large amount of bromoacetate early in the reaction shows

TABLE 5 Product Distributions for Acetolysis of Trihalides **3a–c** at Different Times[a]

Compound	Time (h)	# Runs	 %**6a–c**	 %**7**	 %**8**	cis/trans
3a	5	4	67.2	22.9	9.9	2.3
	10	3	79.2	15.1	5.7	2.6
	20	3	76.5	17.2	6.3	2.7
	40	2	70.7	21.1	8.2	2.6
3b	0.25	2	74.1	17.6	8.3	2.1
	1	2	64.3	22.2	12.5	1.8
	3	3	57.6	27.8	14.6	1.9
	5	2	47.4	31.0	21.6	1.4
	10	2	33.6	44.7	21.2	2.1
	20	3	12.6	55.1	32.3	1.7
3c	5	3	42.7	57.3	0	
	20	4	36.6	63.4	0	

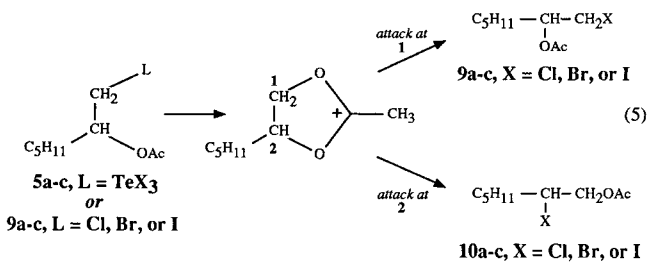
[a]Reaction conditions: Trihalides **3a–c** (1 mmol), dry HOAc (10 mL) refluxed for specified time.

TABLE 6 Product Distributions for Acetolysis of Tribromide **5b** at Different Times[a]

Time (h)	R-CHCH$_2$Br | OAc %**9b**	R-CHCH$_2$OAc | Br %**10b**	R-CHCH$_2$OAc | OAc %**11**
1	59.3	23.1	17.6
3	42.7	26.3	31.0
10	30.8	17.7	51.5
20	13.0	2.4	84.6

[a]Reaction conditions: Trihalide **5b** (1 mmol), dry HOAc (10 mL) refluxed for specified time.

again that the haloacetates are formed first and then react more slowly to form diacetates. Further, the formation of 2-haloheptyl acetates in the solvolysis of trihalides **5a–c** strongly supports the formation of the neighboring group intermediate (Equation 5).



(5)

The Formation of the Diacetates

Longer reaction time for **3a–c** leads to the solvolysis of the first formed haloacetates through the neighboring group intermediate **12** to form a mixture of *cis* and *trans* diacetates. However, *cis* diacetate **7** may also be formed by direct nucleophilic attack of acetate ion on **3a–c** (pathway **E**, Scheme 1). The ratio of *cis* to *trans* diacetate reflects the competition between attack of acetic acid at carbon **3** to give *cis* or attack at carbons **1** or **2** to give *trans* diacetate (Scheme 1). For the solvolysis of **3a** and **3b** in acetic acid, the *cis*/*trans* ratio remains reasonably constant (Table 5). For **3c**, surprisingly, no *trans* diacetate is formed. It has been found that charged nucleophiles cause an increase in attack at carbons **1** and **2** of the neighboring group intermediate [7]. Therefore, the effect of added acetate ion should be to *decrease* the *cis*/*trans* ratio if the formation of the diacetates is only through the neighboring group intermediate **12** (pathway **F**). Table 7 presents data for the solvolysis of **3b** in the presence of differing amounts of lithium acetate. The *cis*/*trans* ratio *increases* substantially. This sharp increase strongly suggests that direct nucleophilic attack by acetate ion at the carbon bearing the trihalotelluro group contributes to the overall solvolysis reaction. For 2-acetoxycyclohexyltellurium triiodide **3c**, no *trans* diacetate forms even in the absence of acetate ion. This suggests that cleavage of the carbon–tellurium bond through direct nucleophilic attack by acetate ion is the exclusive pathway for **3c** because the triiodotelluro group is a much better leaving group than either trichlorotelluro or tribromotelluro.

EXPERIMENTAL

Materials

Tellurium tetrachloride was purchased from Aldrich Chemical Co. and used without further purification.

TABLE 7 Influence of Lithium Acetate on the Acetolysis of Tribromide **3b**[a]

Time (h)	LiOAc mmol	 %**6b**	 %**7**	 %**8**	cis/trans
3	0	57.6	27.8	14.6	1.9
	3	64.7	33.2	2.1	15.8
	5	59.4	35.3	5.3	6.7
	10	56.6	36.9	6.5	5.7
5	0	47.4	31.0	21.6	1.4
	5	64.2	34.4	1.4	24.6
20	0	12.6	55.1	32.3	1.7
	5	37.2	59.0	3.8	15.5

[a]Reaction conditions: Trihalide **3b** (1 mmol), dry HOAc (10 mL) with added LiOAc refluxed for specified time.

Anhydrous lithium acetate was obtained by drying commercial dihydrate (Fluka) in a drying oven for several days.

Instrumentation

Proton and carbon-13 NMR spectra at 200 MHz were recorded on a Varian XL 200E spectrometer with a dual 5 mm switchable probe or on a Varian Gemini 200 spectrometer as solutions in $CDCl_3$. Chemical shifts are reported in δ units downfield from tetramethylsilane. Melting points are uncorrected and were determined on a MEL TEMP melting-point apparatus.

Dry Acetic Acid

Commercial glacial acetic acid from Mallinkrodt Chemical Co. was dried in large quantities. In a typical preparation, 700 mL of glacial acetic acid was treated with 50 mL of acetic anhydride. The mixture was gently refluxed for 3 hours. Fractional distillation yielded the major fraction, about 500 mL, boiling between 117.6 and 118.2°C. Proton NMR spectroscopy showed this material to contain about 3–4% acetic anhydride. "Wet" acetic acid that was used to demonstrate the influence of small amounts of water on the product distribution (Table 3) was the acetic acid fraction that distilled between 116 and 118°C. No acetic anhydride had been added to remove the last traces of water.

Bis(2-acetoxycyclohexyl) Ditelluride

Ditelluride **2** was prepared as previously described [6] from a solution of tellurium tetrachloride (2.69 g, 10.0 mmol) and lithium acetate (2.62 g, 40.0 mmol) in 20 mL of glacial acetic acid that was heated to 80°C to give crude bis(2-acetoxycyclohexyl) ditelluride **2** as an orange oil (1.84 g, 3.4 mmol, 68.5% yield).

2-Acetoxycyclohexyltellurium Trichloride

The crude bis(2-acetoxycyclohexyl) ditelluride (1.84 g, 3.4 mmol) was dissolved in 12 mL of *n*-hexane and 5 mL of carbon tetrachloride. Sulfuryl chloride in carbon tetrachloride (1.17 g in 5 mL of CCl_4) was slowly added to this orange solution. The resulting solution was pale pink to colorless, and the product slowly came out of solution upon standing. The crude product was collected by vacuum filtration and recrystallized from a mixture of *n*-hexane and chloroform (2:1) to give 2-acetoxycyclohexyltellurium trichloride, **3a** (mp 129.1–131.3°C, 1.54 g, 2.8 mmol, 60.4% yield). ^{1}H NMR (200 MHz): δ 1.2–1.5 (m, 2H, CH_2); 1.6–2.1 (m, 3H, CH_2); 2.2–2.5 (m, 2H, CH_2); 2.65–2.8 (m, 1H, CH_2); 2.28 (s, 3H, CH_3CO); 4.22 (ddd, 1H, CHTe, J = 4.7, 10.0, 12.6 Hz); and 5.15 (dt, 1H, CHOAc, J = 5.4, 10.4 Hz). ^{13}C NMR (200 MHz): δ 22.1 (CH_3CO_2); 23.3, 26.1, 27.0, 33.6 (4 CH_2's); 76.6 (CTe); 77.8 (COAc); and 181.5 ($OC(O)CH_3$).

2-Acetoxycyclohexyltellurium Tribromide

2-Acetoxycyclohexyltellurium tribromide was prepared as previously described [6] from crude bis(2-acetoxycyclohexyl) ditelluride (1.47 g, 2.7 mmol) to give 2-acetoxycyclohexyltellurium tribromide **3b** as a yellow solid (mp 111–113°C, 1.99 g, 3.9 mmol 72.2% yield). ^{1}H NMR (200 MHz): δ 1.2–1.5 (m, 2H, CH_2); 1.6–2.1 (m, 3H, CH_2); 2.2–2.6 (m, 2H, CH_2); 2.7–2.85 (m, 1H, CH_2); 2.29 (s, 3H, CH_3CO); 4.40 (ddd, 1H, CHTe, J = 4.8, 9.9, 12.6 Hz); and 5.18 (dt, 1H, CHOAc, J = 5.3, 10.4 Hz). ^{13}C NMR (200 MHz): δ 22.1 (CH_3CO_2); 23.1, 27.5, 28.5, 33.5 (4 CH_2's); 71.6 (CTe); 77.6 (COAc); and 181.3 ($OC(O)CH_3$).

2-Acetoxycyclohexyltellurium Triiodide

The crude bis(2-acetoxycyclohexyl) ditelluride (1.34 g, 2.5 mmol) was dissolved in 60 mL of chloroform. Iodine in carbon tetrachloride (2.04 g, 8.0 mmol in 60 mL of CCl_4) was slowly added to this solution, and the reaction mixture became dark red. The volume of the reaction mixture was reduced under vacuum to approximately 30 mL, and the triiodide crystallized when the solution was allowed to stand overnight in a refrigerator. Recrystallization from

n-hexane:chloroform (2:1) gave 2-acetoxycyclohexyltellurium triiodide **3c** as a dark red/black solid (mp 171.0–174.5°C, 2.15 g, 3.3 mmol, 66.2% yield). ^{1}H NMR (200 MHz): δ 1.3–2.2 (m, 6H, CH_2); 2.6–2.9 (m, 2H, CH_2); 2.30 (s, 3H, CH_3CO); 4.30 (ddd, 1H, CHTe, J = 5.6, 9.9, 11.9 Hz); and 5.22 (dt, 1H, CHOAc, J = 5.3, 10.3 Hz). ^{13}C NMR (200 MHz): δ 21.8 (CH_3CO_2); 22.9, 28.4, 33.4, 33.6 (4 CH_2's); 60.4 (CTe); 76.6 (COAc); and 179.3 ($OC(O)CH_3$).

Bis(2-acetoxyheptyl) Ditelluride

Ditelluride **4** was prepared in the same manner as bis(2-acetoxycyclohexyl) ditelluride using 1-heptene (3.14 g, 32.0 mmol) in place of cyclohexene. The crude bis(2-acetoxyheptyl) ditelluride **4** was isolated as a deep red oil (2.44 g, 4.28 mmol, 85.3% yield).

2-Acetoxyheptyltellurium Trichloride

The crude bis(2-acetoxyheptyl) ditelluride (2.44 g, 4.3 mmol) was dissolved in 10 mL of hexane and 5 mL of chloroform. Sulfuryl chloride (1.17 g, 8.3 mmol in 5 mL of CCl_4) was added dropwise to give a pale yellow solution. After reduction of the volume to 8 mL, 2-acetoxyheptyltellurium trichloride **5a** crystallized as a white solid (mp 91.2–93.3°C, 1.65 g, 4.1 mmol, 48.4% yield). ^{1}H NMR (200 MHz): δ 0.88 (t, 3H, CH_3); 1.2–1.5 (m, 5H, CH_2); 1.6–2.2 (m, 3H, CH_2); 2.28 (s, 3H, CH_3CO); 3.92 (dd, 1H, CH_ATe, J = 2.1, 12.3 Hz); 4.03 (dd, 1H, CH_BTe, J = 9.9, 12.4 Hz); and 5.45 (ddt, 1H, CHOAc, J = 2.1, 12.4, 4.9 Hz). ^{13}C NMR (200 MHz): δ 14.0 (CH_3CH_2); 22.1, (CH_3CO_2); 22.8, 24.6, 31.2, 34.9 (4 CH_2's); 66.9 (CTe); 76.0 (COAc); and 181.6 ($OC(O)CH_3$).

2-Acetoxyheptyltellurium Tribromide

The crude bis(2-acetoxyheptyl) ditelluride (2.84 g, 5.0 mmol) was dissolved in 10 mL of hexane and 5 mL of chloroform. Bromine in carbon tetrachloride (2.47 g, 15.4 mmol in 5 mL of CCl_4) was added dropwise to give a bright yellow solution. After reduction of the volume to 10 mL, 2-acetoxyheptyltellurium tribromide **5b** crystallized as a pale yellow/green solid (mp 86.2–88.7°C, 3.74 g, 7.1 mmol, 71.3% yield). ^{1}H NMR (200 MHz): δ 0.88 (t, 3H, CH_3); 1.2–1.5 (m, 5H, CH_2); 1.6–2.15 (m, 3H, CH_2); 2.27 (s, 3H, CH_3CO); 4.22 (dd, 1H, CH_ATe, J = 2.4, 12.2 Hz); 4.33 (dd, 1H, CH_BTe, J = 9.5, 12.2 Hz); and 5.54 (ddt, 1H, CHOAc, J = 2.4, 12.2, 4.8 Hz). ^{13}C NMR (200 MHz): δ 14.0 (CH_3CH_2); 22.0, (CH_3CO_2); 22.4, 24.5, 31.2, 34.7 (4 CH_2's); 62.6 (CTe); 76.3 (COAc); and 181.4 ($OC(O)CH_3$).

2-Acetoxyheptyltellurium Triiodide

The crude bis(2-acetoxyheptyl) ditelluride (1.94 g, 3.5 mmol) was dissolved in 10 mL of chloroform. Iodine (2.08 g, 8.0 mmol in 25 mL of $CHCl_3$ and 65 mL of CCl_4) was added dropwise to this solution. After the volume of the solution had been reduced to 30 mL under vacuum and allowed to stand overnight, the crude triiodide crystallized and was collected by vacuum filtration. Recrystallization from *n*-hexane:chloroform (2:1) gave 2-acetoxyheptyltellurium triiodide **5c** as a red solid (mp 81–85°C, 2.65 g, 4.0 mmol, 57.1% yield). ^{1}H NMR (200 MHz): δ 0.89 (t, 3H, CH_3); 1.2–2.15 (m, 8H, CH_2); 2.24 (s, 3H, CH_3CO); 4.38 (dd, 1H, CH_ATe, J = 9.6, 12.0 Hz); 4.48 (dd, 1H, CH_BTe, J = 2.1, 12.0 Hz); and 5.63 (ddt, 1H, CHOAc, J = 2.2, 12.3, 4.9 Hz). ^{13}C NMR (200 MHz): δ 14.0 (CH_3CH_2); 21.5, (CH_3CO_2); 22.4, 24.5, 31.3, 34.4 (4 CH_2's); 52.6 (CTe); 76.8 (COAc); and 179.9 ($OC(O)CH_3$).

trans-2-Acetoxy-1-bromoocyclohexane

trans-2-Bromocyclohexanol was prepared by reaction of cyclohexene and water in dimethyl sulfoxide with N-bromosuccinimide [11]. The crude *trans*-2-bromocyclohexanol was acylated with pyridine/acetic anhydride to yield *trans*-2-acetoxy-1-bromoocyclohexane **6b** (4.32 g, 19.5 mmol, 90.1% yield). ^{1}H NMR (200 MHz): δ 1.2–1.5 (m, 3H, CH_2); 1.6–2.1 (m, 4H, CH_2); 2.2–2.5 (m, 1H, CH_2); 2.02 (s, 3H, CH_3CO); 3.90 (ddd, 1H, CHBr, J = 4.4, 9.2, 10.8 Hz); and 4.82 (dt, 1H, CHOAc, J = 4.7, 9.3 Hz). ^{13}C NMR (200 MHz): δ 21.1 (CH_3CO_2); 23.3, 25.6, 31.2, 35.7 (4 CH_2's); 52.9 (CBr); 75.8 (COAc); and 170.0 ($OC(O)CH_3$).

Cyclohexene Oxide

trans-2-Bromocyclohexanol (4.32 g, 22.0 mmol) was dissolved in 75 mL of diethyl ether. To this solution was added 40 mL of 5 M sodium hydroxide solution, and the heterogeneous mixture was stirred for 2 hours. The organic layer was separated and dried over potassium carbonate. The solvent was removed under vacuum to yield crude cyclohexene oxide as a colorless oil (1.72 g, 80.0% yield).

trans-2-Acetoxy-1-chlorocyclohexane

A solution of crude cyclohexene oxide (2.21 g, 22.5 mmol) in 50 mL of diethyl ether was stirred with 50 mL 5 M HCl for 2 hours. The organic layer was separated, dried over potassium carbonate, and the solvent removed under vacuum. The *trans*-2-chlorocy-

clohexanol was acylated with pyridine/acetic anhydride to yield *trans*-2-acetoxy-1-chlorocyclohexane **6a** (1.93 g, 10.9 mmol, 48.1% yield). ^{1}H NMR (200 MHz): δ 1.2–1.5 (m, 3H, CH_2); 1.6–1.95 (m, 4H, CH_2); 2.1–2.3 (m, 1H, CH_2); 2.02 (s, 3H, CH_3CO); 3.77 (ddd, 1H, CHCl, J = 4.4, 9.1, 10.4 Hz); and 4.74 (dt, 1H, CHOAc, J = 4.7, 9.3 Hz). ^{13}C NMR (200 MHz): δ 21.0 (CH_3CO_2); 23.2, 24.5, 30.7, 34.8 (4 CH_2's); 60.7 (CBr); 75.8 (COAc); and 170.1 ($OC(O)CH_3$).

trans-2-Acetoxy-1-iodocyclohexane

A solution of crude cyclohexene oxide (2.13 g, 21.7 mmol) in 50 mL of diethyl ether was stirred with potassium iodide (4.00 g) and 0.5 mL of nitric acid dissolved in 50 mL of water for 3 hours. The organic layer was separated, dried over magnesium sulfate, and the solvent removed under vacuum. The *trans*-2-iodocyclohexanol was acylated with acetic anhydride and a few drops of nitric acid to yield *trans*-2-acetoxy-1-iodocyclohexane **6c** (4.43 g, 16.5 mmol, 75.9% yield). ^{1}H NMR (200 MHz): δ 1.2–1.6 (m, 4H, CH_2); 1.7–1.9 (m, 3H, CH_2); 2.3–2.45 (m, 1H, CH_2); 2.03 (s, 3H, CH_3CO); 4.00 (ddd, 1H, CHI, J = 4.3, 9.5, 11.2 Hz); and 4.83 (dt, 1H, CHOAc, J = 4.4, 9.5 Hz). ^{13}C NMR (200 MHz): δ 21.2 (CH_3CO_2); 23.5, 27.0, 31.6, 31.8 (4 CH_2's); 37.8 (CI); 76.7 (COAc); and 176.7 ($OC(O)CH_3$).

Acetolysis of 2-Acetoxyalkyltellurium Trihalides **3a–c** *and* **5a–c**

In a typical experiment, 2-acetoxycyclohexyltellurium trichloride **3a** (0.375 g, 1.0 mmol) was dissolved in 10.0 mL of dry acetic acid to give a homogeneous solution. The reaction mixture was heated to 120°C and refluxed at this temperature for 5 hours. The reaction mixture was then cooled to room temperature and the solid tellurium removed by filtration. The filtrate was diluted with 15 mL of saturated brine and then extracted with diethyl ether (3 × 20 mL). The combined ether extracts were washed with aqueous sodium bicarbonate (8 × 15 mL) and the organic layer dried over magnesium sulfate. The solvent was removed under vacuum to yield a yellow oil (0.135 g, 76.7% yield). Proton NMR spectroscopy showed this oil to be a mixture of *cis*-1,2-diacetoxycyclohexane **7** (21.3%), *trans*-1,2-diacetoxycyclohexane **8** (10.5%), and *trans*-2-chlorocyclohexyl acetate **6a** (68.3%).

This procedure was used for the acetolysis experiments reported in Tables 3–7 except that different times of reflux may have been used. For the acetolysis experiments presented in Table 7, the cited amount of anhydrous lithium acetate was added to the reaction mixture. For the acetolysis of trihalides **3a–c** after different times (Table 4), the relative yields are the average of several experiments. These averages show that the relative yields are reproducible to about ±4%. For example, the four runs for the acetolysis of 2-acetoxycyclohexyltellurium trichloride **3a** for 5 hours gave 21.3, 32.1, 18.2, and 20.1% *cis*-1,2-diacetoxycyclohexane **7;** 10.5, 9.1, 10.6, and 9.3% *trans*-1,2-diacetoxycyclohexane **8;** and 68.3, 58.8, 71.2, and 70.6% *trans*-2chlorocyclohexyl acetate **6a.**

Proton NMR Determination of Product Distributions

Product distributions in the acetolyses of tellurium trihalides were determined from the integration of the appropriate resonances in the proton NMR spectrum of the product mixture. The proton signals for the hydrogens attached to the halocarbon (Table 1, H_1) for the *trans*-2-acetoxyl-halocyclohexylacetates did not overlap with other resonances and were used to determine the relative amounts of **6a–c.** Similarly, the resonance due to hydrogens attached to the acetoxy carbons of *cis*-1,2-diacetoxycyclohexane was free of overlap and used to measure the amount of **7** in the product mixture. The proton signal for the acetoxy hydrogens of *trans*-1,2-diacetoxycyclohexane overlapped with the acetoxy hydrogens of **6a–c.** Therefore, the amount of **8** was determined by subtracting the halocarbon H_1 integral from the total integral in the δ 4.65–4.85 region.

The protons on carbon **1** of the 2-acetoxy-1-haloheptanes **9a–c** appeared in the region between δ 3.18 and 3.59 and did not overlap with any other proton resonances (Table 2). Therefore, the integral of these protons was used to determine the relative amount of **9a–c** in the acetolysis of 2-acetoxyheptyltellurium trihalides **5a–c.** The resonance for the proton on carbon **2** of 1,2-diacetoxyheptane **11** appears at δ 4.96 and overlaps the resonances for hydrogen of the 2-acetoxy-1-haloheptanes **9a–c.** Therefore, the relative amount of **11** was determined by subtracting the normalized integral for the 2-acetoxy-1-haloheptanes from the integral in the region between δ 4.88 and 5.08. Protons on carbons **1** and **2** for the 1-acetoxy-2-haloheptanes **10a–c** overlap with the protons on carbon **1** of diacetate **11** in the region between δ 3.85 and 4.25. Therefore, the relative amount of **10a–c** was estimated by subtracting the normalized integral for 1,2-diacetoxyheptane from the integral between δ 3.85 and 4.25.

Oxidation of Cyclohexene and 1-Heptene with Tellurium Tetrachloride

Cyclohexene (1.05 g, 12.8 mmol) was added by syringe to a mixture of tellurium tetrachloride (1.39 g,

5.1 mmol) and lithium acetate (1.01 g, 15.3 mmol) in 20 mL of dry acetic acid. The mixture was heated to 80°C for 1 hour to give a homogeneous solution, and then the temperature was raised to 120°C for 20 hours. The reaction mixture was cooled to room temperature and the solid tellurium filtered off. The filtrate was diluted with 20 mL of saturated brine and then extracted with diethyl ether (3 × 20 mL). The combined ether extracts were washed with water (8 × 15 mL) and then dried over magnesium sulfate. The solvent was removed under vacuum to yield a yellow oil (1.030 g, 5.15 mmol, 100% yield based upon $TeCl_4$). Proton NMR spectroscopy showed this oil to be a mixture of *trans*-2-chlorocyclohexyl acetate **6a** (79.5%), *cis*-1,2-diacetoxycyclohexane **7** (15.3%), and *trans*-1,2-diacetoxycyclohexane **8** (5.2%). In a similar manner, 1-heptene (1.05 g, 10.6 mmol) was reacted with a mixture of tellurium tetrachloride (1.35 g, 5.0 mmol) and lithium acetate (0.85 g, 12.9 mmol) in 20 mL of dry acetic acid to yield a yellow oil (1.40 g, 7.08 mmol). Proton NMR spectroscopy showed this oil to be a mixture of 2-acetoxy-1-chloroheptane **9a** (47.3%), 2-chloro-1-acetoxyheptane **10a** (42.0%), and 1,2-diacetoxyheptane **11** (10.7%).

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