ORGANOMETALLICS

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Organometallics, **1990**, 9 (12), 3073-3080• DOI: 10.1021/om00162a019 • Publication Date (Web): 01 May 2002

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Acetoxytellurination of Alkenes with Tellurium Tetrachloride and Lithium Acetate

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Received June 19, 1990

The reaction of alkenes with tellurium tetrachloride and lithium acetate in acetic acid at 120 °C for 20 h afforded the *vic*-diacetates in good yields. Only the *cis*-diacetate was obtained in the diacetoxylation of cyclohexene. With *cis*- and *trans*-2-butenes, syn stereochemistry is preferred (syn/anti = 92/8 and 84/6). When the addition is carried out at 80 °C for 3 h and the reaction mixture then reduced with aqueous sodium thiosulfate, bis(2-acetoxyalkyl)ditellurides are isolated in moderate to good yield. One to one adducts (tellurium–alkene) are produced with all alkenes except vinyl acetate without contamination from 1:2 adducts even when the reaction is carried out in the presence of excess alkene. Acetoxytellurination of alkenes is completely anti stereospecific for internal alkenes and regioselective (Markovnikov adducts) for terminal alkenes. An ionic mechanism involving a telluronium ion intermediate is suggested for the addition reaction. The acetoxyalkyl ditellurides were converted to (acetoxyalkyl)tellurium tribromides with bromine in chloroform. The reaction of the (acetoxyalkyl)tellurium tribromides with acetic acid at 120 °C to give diacetates was used as a model for the second step of the diacetoxylation reaction. The stereochemistry of the diacetates formed in the reaction of the tribromides with acetic acid depended upon structure. (2-Acetoxycyclopentyl)tellurium tribromide gave a 23:77 mixture of *cis*- and *trans*-diacetates, while (2-acetoxycyclohexyl)tellurium tribromide in the presence of added acetate gave exclusively the *cis*-diacetate. The loss of stereoselectivity in the acetoxylation of the tribromides and in the second step of the diacetoxylation reaction is due to a competition between rearward attack by acetate at the tellurium carbon and neighboring acetoxy participation.

Introduction

Tellurium(IV) oxide (TeO_2) is sparingly soluble in many common organic solvents and therefore almost inactive in the oxidation of organic compounds in homogeneous solution. However, when TeO_2 is solubilized with lithium halides (eq 1; X = Cl, Br) in acetic acid, it has been found

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

to be an efficient reagent for the oxidation of alkenes to *vic*-diacetates,[1,2] for selective 1,4-diacetoxylation of 1,3-conjugated dienes,[3] and for the oxidation of aromatic and carbonyl compounds.[4] The structure of the solubilized tellurium(IV) species taking part in these reactions is unknown. It has been proposed that this species is a mixed halide–acetate complex (1). However, experimental evidence for the exact structure is still lacking.

In the first step of the proposed mechanism for the oxidation of alkenes to *vic*-diacetates, a tellurium(IV) species such as 1 electrophilically attacks the carbon–carbon π bond to form a (β-haloalkyl)- or (β-acetoxyalkyl)tellurium(IV) compound. This species was first suggested by Bergman and Engman as an intermediate in the oxidation of alkenes[1] and in the oxidative cyclization of γ- and δ-hydroxyalkenes by the TeO_2–HOAc–LiX system.[5] In the second step of the mechanism, the carbon–tellurium bond is oxidatively cleaved by acetate. The nature of the oxidative cleavage step has been investigated with use of 2-acetoxycyclohexyl phenyl telluride as a model compound in the reaction.[2]

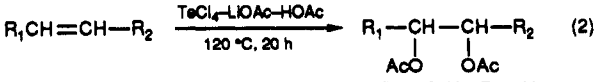
Table I. Diacetoxylation of Alkenes with $TeCl_4$ and LiOAc[a]

entry no.	alkene	product	isolated yield, %[b]	isomer ratio[c]
1	cyclopentene	2	42	cis/trans = 38/62
2	cyclohexene	3	35	cis only
3[d]	cyclohexene	3	50	cis only
4	1-hexene	4	21	
5[d]	1-hexene	4	49	
6	styrene	5	45	
7[d]	styrene	5	54	
8	*cis*-2-butene	6	34	meso/*dl* = 92/8
9	*trans*-2-butene	6	24	meso/*dl* = 16/84

[a] Amounts of reactants: alkene (10 mmol), $TeCl_4$ (5 mmol), LiOAc (20 mmol), AcOH (15 mL). [b] Yield based on $TeCl_4$. [c] Determined by ^{13}C NMR spectroscopy. [d] $TeBr_4$ (5 mmol) used instead of $TeCl_4$.

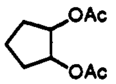
Results and Discussion

Diacetoxylation of Alkenes. We have carried out the diacetoxylation of alkenes with a solution of tellurium tetrachloride ($TeCl_4$) and lithium acetate (LiOAc) in acetic acid. When a mixture of $TeCl_4$ and anhydrous LiOAc in acetic acid was stirred at 80 °C, the mixture became homogeneous within about 1 h, probably forming a mixed chloride–acetate complex such as 1. Alkenes were added to this homogeneous solution, and the solution was heated to 120 °C for 20 h (eq 2). During this time elemental tellurium was deposited as a black precipitate.[1,2] Results



$$R_1CH{=}CH{-}R_2 \xrightarrow[120\ ^\circ C,\ 20\ h]{TeCl_4-LiOAc-HOAc} R_1{-}\underset{AcO}{CH}{-}\underset{OAc}{CH}{-}R_2 \qquad (2)$$

4: $R_1 = C_4H_9$, $R_2 = H$
5: $R_1 = C_6H_5$, $R_2 = H$
6: $R_1 = CH_3$, $R_2 = CH_3$



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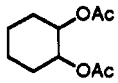

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(1) Bergman, J.; Engman, L. *J. Organomet. Chem.* **1979,** *181,* 335.
(2) Uemura, S.; Ohe, K.; Fukuzawa, S.; Patil, S. R.; Sugita, S. *J. Organomet. Chem.* **1986,** *316,* 67.
(3) (a) Uemura, S.; Fukuzawa, S.; Patil, S. R.; Okano, M. *J. Chem. Soc., Perkin Trans. 1* **1985,** 499. (b) Uemura, S.; Fukuzawa, S.; Okano, M. *Tetrahedron Lett.* **1981,** 5331.
(4) Bergman, J.; Engman, L. *J. Org. Chem.* **1982,** *47,* 5191.
(5) Bergman, J.; Engman, L. *J. Am. Chem. Soc.* **1981,** *103,* 5196.

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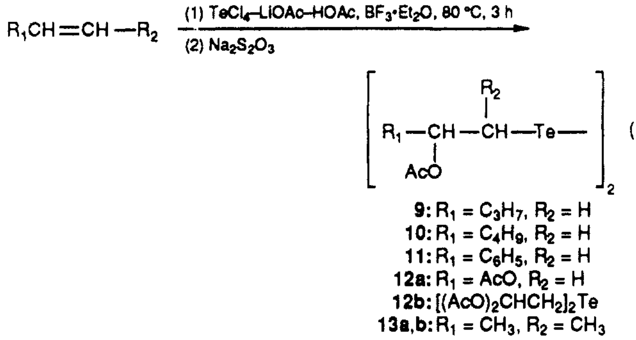
for the diacetoxylation reactions of cyclopentene, cyclohexene, 1-hexene, styrene, and *cis*- and *trans*-butenes are shown in Table I. *vic*-Diacetates were produced in good yield, and the overall stereochemistry of the addition and oxidative-cleavage reactions was dominantly syn except for cyclopentene. These results are very similar to those for the oxidations of alkenes with the TeO_2–LiX–HOAc system.[1,2] Cyclohexene gave only the cis isomer of **3** (Table I, entry 2), and *cis*- and *trans*-2-butene afforded mainly the meso and *dl* isomers of **6**, respectively (entries 8 and 9). With cyclopentene the *vic*-diacetate was a mixture of cis and trans isomers of **2** in a ratio of 38:62 (entry 1), while the TeO_2–LiX–HOAc system gave the cis isomer only. Tellurium tetrabromide could be used in the place of $TeCl_4$ with LiOAc in the diacetoxylation reactions (entries 3, 5, and 7).

Acetoxytellurination of Alkenes. Alkenes were reacted with a homogeneous solution of $TeCl_4$ and LiOAc dissolved in acetic acid in the presence of boron trifluoride etherate (BF_3·Et_2O) at 80 °C for 3 h. During this time no diacetate formation took place and very little elemental tellurium precipitated. After 3 h, the reaction mixtures were treated with sodium thiosulfate and acetoxyalkyl ditellurides **7**–**13** were isolated (eq 3). It is important to note that the intermediates were reduced to the ditellurides. (2-Chloroalkyl)tellurium compounds are known to undergo reductive elimination to produce the original alkene and elemental tellurium with reducing agents such as sodium sulfide.[6] It has been proposed that such reductive eliminations require a good leaving group such as chloride *β* to tellurium. With poorer leaving groups such as acetoxy and alkoxy *β* to tellurium, ditellurides are formed without elimination.[7,8] Recently Engman prepared bis(*β*-alkoxyalkyl) ditellurides through a similar reaction, the alkoxytellurination of alkenes with tellurium dioxide in alcoholic aqueous hydrochloric acid followed by reduction with sodium disulfite.[9]



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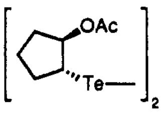

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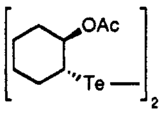

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The acetoxytellurination of cyclohexene under a variety of conditions is summarized in Table II. 1,1′-Bis(2-acetoxycyclohexyl) ditelluride (**8**) is assigned trans stereochemistry on the basis of a large vicinal coupling between the methine hydrogen on the acetate carbon and the methine hydrogen on the tellurium carbon ($^3J_{H-H}$ = 10.2 Hz). Reaction times of more than 3 h had little effect on the yield (entries 1 and 2). In the absence of BF_3·Et_2O, the yield was somewhat lower (entry 3). The use of $TeCl_4$ alone did not give **8** (entry 4), showing that the presence of LiOAc is critical in the acetoxytellurination reaction. The combination of $TeBr_4$ with LiOAc did not give **8** (entry 5), even though this reagent gave a 50% yield of the diacetate when the reaction was carried out at 120 °C. Lower yields of **8** were obtained when TeO_2–LiCl was used (entries 6 and 7), and no **8** was obtained if TeO_2–LiBr was used (entry 8). Interestingly, ammonium hexachlorotellurate could be used in place of $TeCl_4$ (entry 9). In all of these reactions tellurium(IV) adds only once to cyclohexene. Reduction of this 1:1 adduct with sodium thiosulfate gave the ditelluride **8**. No monotelluride was formed even when an excess of cyclohexene was used. No reaction occurred when acetic acid was replaced by other organic solvents such as chloroform and acetonitrile.

Table II. Acetoxytellurination of Cyclohexene with Te(IV) Reagents[a]

entry no.	Te compd	Li salt (amt, mmol)	isolated yield of 8,[b] %
1	$TeCl_4$	LiOAc (40)	42
2[c]	$TeCl_4$	LiOAc (40)	45
3[d]	$TeCl_4$	LiOAc (40)	32
4	$TeCl_4$	none	0
5	$TeBr_4$	LiOAc (40)	0
6	TeO_2	LiCl (100)	18
7[d]	TeO_2	LiCl (100)	8
8	TeO_2	LiBr (100)	0
9	$(NH_4)_2TeCl_6$	LiOAc (60)	36

[a] Cyclohexene (10 mmol), the tellurium compound (10 mmol), BF_3·Et_2O (10 mmol), and AcOH were reacted at 80 °C for 3 h and then treated with $Na_2S_2O_3$. [b] Yield based on tellurium compounds. [c] Reaction time 20 h. [d] No BF_3·Et_2O.

Table III. Acetoxytellurination of Alkenes with $TeCl_4$ and LiOAc[a]

entry no.	alkene (amt, mmol)	product	isolated yield, %[b]
1	cyclopentene	**7**	41
2	cyclohexene	**8**	42
3	1-pentene	**9**	58
4	1-hexene	**10**	64
5	styrene	**11**	52
6	vinyl acetate (10)	**12a**	30
7	vinyl acetate (50)	**12b**	65
8	*cis*-2-butene (40)	**13a**	43
9	*trans*-2-butene (40)	**13b**	48

[a] Alkene (20 mmol), $TeCl_4$ (10 mmol), LiOAc (40 mmol), BF_3·Et_2O (10 mmol), and AcOH (20 mL) were reacted at 80 °C for 3 h and then treated with $Na_2S_2O_3$. [b] Yield based on $TeCl_4$.

The acetoxytellurination of other alkenes was carried out with use of $TeCl_4$–LiOAc and BF_3·Et_2O at 80 °C for 3 h followed by treatment with aqueous sodium thiosulfate. The results are shown in Table III. The products of the reduction with $Na_2S_2O_3$ were acetoxyalkyl ditellurides rather than tellurides, even though a 1:2 molar ratio of $TeCl_4$ to alkene was used except for the product of the reaction of vinyl acetate. Ditellurides resulted from the reduction of 1:1 adducts between **1** and alkenes. Vinyl acetate gave a mixture of ditelluride (**12a**) from the reduction of the 1:1 adduct and telluride (**12b**) from the reduction of the 1:2 adduct. Equimolar amounts of vinyl acetate and $TeCl_4$ were required to obtain only the ditelluride, while a large excess of vinyl acetate afforded the telluride (Table III, entries 6 and 7). Cyclic and acyclic alkenes gave the corresponding acetoxyalkyl ditellurides in moderate to good yield. However, with sterically more crowded alkenes such as *α*-methylstyrene, *trans*-stilbene,

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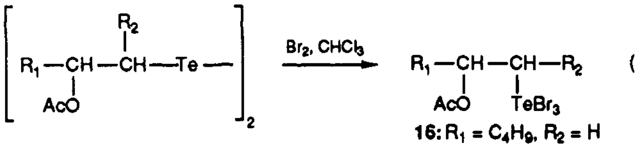
(6) (a) Bäckvall, J.-E.; Bergman, J.; Engman, L. *J. Org. Chem.* **1983**, *48*, 3918. (b) Bäckvall, J.-E.; Engman, L. *Terahedron Lett.* **1981**, 1919.

(7) Engman, L. *J. Am. Chem. Soc.* **1984**, *106*, 3977.

(8) (a) Uemura, S.; Fukuzawa, S.; Toshimitsu, A. *J. Organomet. Chem.* **1983**, *250*, 203. (b) Uemura, S.; Fukuzawa, S.; Toshimitsu, A.; Okano, M. *Tetrahedron Lett.* **1982**, 1177.

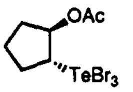
(9) Engman, L. *Organometallics* **1989**, *8*, 1997.

and 2-methyl-2-butene, no ditellurides were obtained. The acetoxyalkyl ditellurides were stable at room temperature in the air for a few weeks. They gradually decomposed over longer periods with the deposition of elemental tellurium. The acetoxyalkyl ditellurides were reacted with bromine to give high yields of (acetoxyalkyl)tellurium tribromides 14–18 (eq 4). The (acetoxyalkyl)tellurium tribromides were used to show that the stereochemistry of the addition reaction was anti and to study the oxidative cleavage reaction.



$$\left[R_1\text{—}\underset{\text{AcO}}{\text{CH}}\text{—}\overset{R_2}{\text{CH}}\text{—Te—}\right]_2 \xrightarrow{Br_2,\ CHCl_3} R_1\text{—}\underset{\text{AcO}}{\text{CH}}\text{—}\underset{TeBr_3}{\text{CH}}\text{—}R_2 \qquad (4)$$

16: $R_1 = C_4H_9$, $R_2 = H$
17: $R_1 = C_6H_5$, $R_2 = H$
18a,b: $R_1 = CH_3$, $R_2 = CH_3$



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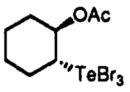

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Magnetic Resonance Spectra of Acetoxyalkyl Ditellurides and (Acetoxyalkyl)tellurium Tribromides. Spectral and analytical data for the acetoxyalkyl ditellurides and (acetoxyalkyl)tellurium tribromides are summarized in Tables IV and V. The proton and carbon-13 spectra of ditellurides 7–13 and tribromides 14–18 were used to characterize these new compounds. The ditellurides displayed resonances between δ 3.20 and 3.70 for the protons on the carbon attached to tellurium. In the tribromides, these hydrogens are deshielded by the electron-withdrawing influence of the bromines and appear between δ 4.26 and 4.60. The protons on the acetoxy carbon are between δ 4.65 and 5.10 in the ditellurides and somewhat further downfield in the tribromides between δ 5.20 and 5.90.

In the acetoxytellurination of cyclic and internal alkenes (cyclohexene, cyclopentene, and *cis*- and *trans*-2-butene), the alkene carbons become chiral. If the addition happens in an anti manner, ditellurides 7, 8, 13a, and 13b will be mixtures of two diastereomers. These mixtures of diastereomeric ditellurides were not separated. The proton and carbon-13 spectra were complicated because of the close-lying resonances for the two diastereomers. For ditelluride 8, separate resonances for each carbon of both diastereomers were observed. For 9 and 10, only 10 of 14 and 11 of 16 carbon-13 resonances were resolved even at 400 MHz. For 13a and 13b, separate carbon-13 resonances were not observed for carbons 1 and 3 of 13a, for carbon 4 and the acetoxy methyl carbon of 13b, or for both the acetoxy carbonyl carbons.

In the proton spectra, separate resonances for the same proton in each diastereomer were often not observed even at 400 MHz, particularly for coupled methyl and methylene protons. The protons on the acetoxy carbons of 8 were found to be two overlapping doublets of triplets due to a small coupling to the equatorial hydrogen on carbon 3 of 4.3 Hz and to large vicinal couplings of 10.2 Hz to the axial hydrogens on carbon 3 and to the hydrogen on the tellurium carbon. This complex pattern was simulated by using the chemical shifts and coupling constants presented in Table IV. The protons on the tellurium carbons of the two diastereomers of 8 were not resolved but appeared as a slightly broadened doublet of triplets. For 13a and 13b, the protons on the acetoxy carbons and on the tellurium carbons were overlapping doublets of quartets. These complex multiplets were well enough resolved at 400 MHz to determine the chemical shifts and couplings for each proton in both diastereomers (Table IV).

The ditellurides from terminal alkenes (1-pentene, 1-hexene, and styrene) were also mixtures of diastereomers because the acetoxy carbon is chiral and two chiral carbons are joined by a tellurium–tellurium bond. The carbon-13 spectra showed resolved resonances for the carbons attached to tellurium and for the acetoxy carbons for each diastereomer of 9 and 10, but only one carbonyl carbon was observed, and all the methylene and methyl resonances were not resolved. The proton spectra for 9, 10, and 11 were further complicated because the protons on the tellurium carbon are diastereotopic (Table IV, H_a and H_b). For 9 and 10, two overlapping doublets of doublets were observed for H_a and two overlapping multiplets (2 × 2 × 3, ddt) were observed for the hydrogens on the acetoxy carbons. However, the H_b hydrogens were accidentally equivalent, and one doublet of doublets was observed. The chemical shifts and coupling constants obtained from simulations of these patterns are presented in Table IV.

Tellurium-125 magnetic resonance confirmed the presence of diastereomeric ditellurides. Two ^{125}Te resonances were observed with slightly different chemical shifts for the diastereomeric telluriums of 8, 10, 11, 13a, and 13b (Table IV). The tellurium shifts are in the range expected for dialkyl ditellurides.[10]

The magnetic resonance spectra of the tribromides were somewhat simpler than for the ditellurides because single compounds rather than mixtures of diastereomers were present. The spectral and analytical data for (acetoxyalkyl)tellurium tribromides 14–18 are presented in Table V.

Stereochemistry of the Addition Reaction. The stereochemistry of the addition of 1 to acyclic alkenes was determined by investigating the acetoxytellurination of *cis*- and *trans*-2-butenes. No stereochemical information could be obtained from the proton NMR spectra of the ditellurides from *cis*- and *trans*-2-butenes, 13a and 13b. The vicinal couplings between the methine hydrogens were the same size for both ditellurides (5.2 Hz, Table IV).

Bromination of 13a and 13b gave (acetoxylalkyl)tellurium tribromides 18a and 18b in high yield (eq 4). The stereochemistry at the tellurium carbon and the acetoxy carbon was not changed in this reaction. Therefore, the size of the vicinal proton–proton coupling between the methine hydrogen on the tellurium carbon and the methine hydrogen on the acetoxy carbon in tribromides 18a and 18b was used to determine the stereochemistry of the addition. It has previously been reported that the vicinal couplings for the threo isomers of the $TeCl_4$ adducts of alkenes are larger than the vicinal couplings for the erythro isomers.[6] This is based on the assumption that the tellurium prefers to be gauche to the chlorine and anti to the alkyl group. In this preferred conformation, chlorine can donate electron density to the electrophilic tellurium atom and steric interference with the alkyl group is minimized. Favored gauche conformations have also been proposed to account for proton couplings for compounds in which oxygen[5] or acyloxy groups[7] are β to tellurium. An adjacent tellurium also has a large effect on the carbonyl frequencies, lowering them by about 110 cm^{-1} to between 1605 and 1630 cm^{-1}.[7,11]

In (acetoxyalkyl)tellurium tribromides 18a and 18b, it is reasonable to expect a similar interaction between the electron-deficient tellurium and the electron-rich acetoxy

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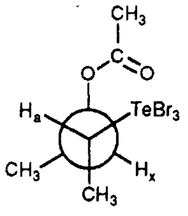
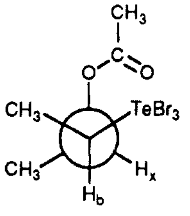
(10) O'Brien, D. H.; Dereu, N.; Grigsby, R. A.; Irgolic K. J. *Organometallics* **1982**, *1*, 513.

(11) (a) Engman, L.; Cava, M. P. *J. Org. Chem.* **1981**, *46*, 4194. (b) Piette, J. L.; Thibaut, P.; Renson, M. *Tetrahedron* **1978**, *34*, 655.

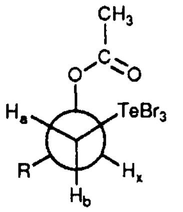
group. The effect of electron donation by the acetoxy group toward tellurium in the tribromides is seen in the infrared spectra. The acetoxy carbonyls of ditellurides **13a** and **13b** are at about 1730–1740 cm^{-1}, compared to 1640–1650 cm^{-1} for tribromides **18a** and **18b**. Tribromide **18a**, obtained from *cis*-2-butene via bromination of the mixture of diastereomeric ditellurides **13a**, has a large vicinal coupling of 9.2 Hz, and therefore, **13a** and **18a** are threo isomers. Tribromide **18b**, obtained from **13b**, has a small vicinal coupling constant of 1.6 Hz. Therefore, **13b** and **18b** are assigned erythro stereochemistry. The terminal tribromides **16** and **17** also have favored gauche conformations as shown by one large and one small vicinal coupling constant. Obtaining the threo tribromide from *cis*-2-butene and the erythro tribromide from *trans*-2-butene shows that the stereochemistry of acetoxytellurination of acyclic alkenes is anti.



18a, (threo): $^3J_{H_a-H_x}$ = 9.2 Hz



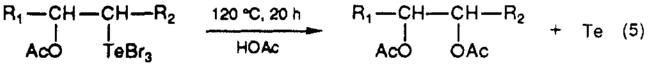
18b, (erythro): $^3J_{H_b-H_x}$ = 1.6 Hz



16: R = *n*-C_4H_9; $^3J_{H_a-H_x}$ = 10.3 Hz, $^3J_{H_b-H_x}$ = 1.7 Hz
17: R = C_6H_5; $^3J_{H_a-H_x}$ = 10.6 Hz, $^3J_{H_b-H_x}$ = 1.6 Hz

The stereochemistry of addition of **1** to cyclic alkenes is also anti. As already noted, the ditelluride from cyclohexene, **8**, displays a large vicinal coupling of 10.2 Hz and is therefore the trans isomer. The products obtained from acetoxytellurination and bromination of cyclopentene and cyclohexene, **14** and **15**, contained single isomers with large vicinal coupling constants ($^3J_{H-H}$ = 8.7 and 10.0 Hz, respectively), and therefore, **14** and **15** are trans isomers. Consequently, the ditellurides from acyclic and cyclic alkenes were formed through an anti stereospecific addition of acetoxy and tellurium to the alkene.

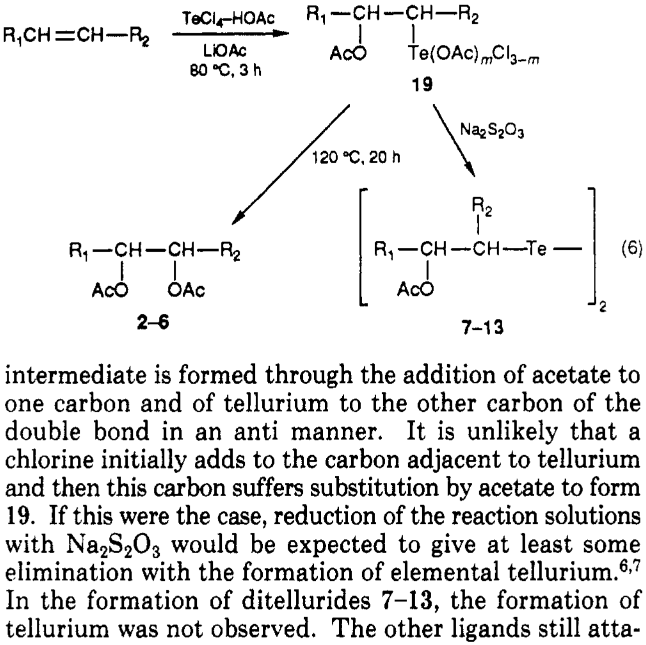
Oxidative Cleavage of the Carbon–Tellurium Bond. In the second step of the diacetoxylation reaction, the tellurium moiety is displaced by an acetoxy group. The (acetoxyalkyl)tellurium tribromides were used to study the stereochemistry of this step (eq 5). The results of the reactions of tribromides **14–18** with acetic acid under conditions identical with those of the diacetoxylation reaction are shown in Table VI. If the oxidative cleavage reaction occurs through rearward attack by acetate on the tellurium carbon, trans tribromides **14** and **15** should yield cis diacetates, threo tribromide **18a**, a meso diacetate, and erythro tribromide **18b**, a *dl* diacetate. These expectations were not realized. In the absence of LiOAc, tribromides **14** and **15** gave cis/trans mixtures of **2** and **3** (entries 1 and 3). For (2-acetoxycyclopentyl)tellurium tribromide (**14**), the amount of *trans*-diacetate was more than 3 times greater than the amount of *cis*-diacetate! The threo and erythro isomers of **18** gave mixtures of meso and *dl* isomers of **6** (entries 8 and 10). Addition of LiOAc dramatically changed the stereospecificity and improved the yields. (2-Acetoxycyclohexyl)tellurium tribromide (**15**) afforded only the cis isomer of **3** (entry 4). The threo isomer of **18** produced mainly meso-**6**, while the erythro isomer of **18** gave mainly *dl*-**6** (entries 9 and 11). However, reaction of (2-acetoxycyclopentyl)tellurium tribromide (**14**) in the presence of LiOAc still gave a mixture of **2** greater than 50% trans (entry 2).



$$R_1\underset{AcO}{CH}-\underset{TeBr_3}{CH}-R_2 \xrightarrow[HOAc]{120\ ^\circ C,\ 20\ h} R_1-\underset{AcO}{CH}-\underset{OAc}{CH}-R_2 + Te \quad (5)$$

14–18 **2–6**

Mechanism of the Diacetoxylation of Alkenes. On the basis of the evidence presented here and given in previous investigations, it is clear that the oxidation of alkenes with tellurium reagents is a two-step process. In the first step, tellurium adds to one carbon of the double bond. Trapping the intermediate as the ditelluride in the acetoxytellurination reaction shows that it is most likely that acetoxy adds to the other carbon of the double bond. The acetoxyalkyl ditellurides **7–13** were formed under conditions milder than those required for diacetoxylation of alkenes. For example, cyclohexene gave ditelluride **8** when the reaction solution was reduced with sodium thiosulfate after only 3 h at 80 °C but 120 °C for 20 h was required to obtain *cis*-1,2-diacetoxycyclohexane (**3**). This evidence strongly suggests that the reaction solutions contain a common intermediate such as **19** in the diacetoxylation and acetoxytellurination reactions (eq 6). This intermediate is formed through the addition of acetate to one carbon and of tellurium to the other carbon of the double bond in an anti manner. It is unlikely that a chlorine initially adds to the carbon adjacent to tellurium and then this carbon suffers substitution by acetate to form **19**. If this were the case, reduction of the reaction solutions with $Na_2S_2O_3$ would be expected to give at least some elimination with the formation of elemental tellurium.[6,7] In the formation of ditellurides **7–13**, the formation of tellurium was not observed. The other ligands still attached to tellurium remain uncertain. If **19** is a common intermediate, the evidence presented here for the acetoxytellurination of cyclohexene, cyclopentene, and *cis*- and *trans*-2-butene shows that the stereochemistry of addition for the first step of diacetoxylation of alkenes is anti.



Previous investigations of the *overall* stereochemistry of diacetoxylation of alkenes show that syn addition is preferred.[1,2,8,12] Likewise, we have found that the *overall* stereochemistry of diacetoxylation shows a preference for syn addition (Table I). The formation of ditellurides **7**, **8**, **13a**, and **13b** occurred in an anti manner. This stereochemistry for the addition step is consistent with the previously suggested telluronium ion mechanism (eq 7).[6] The telluronium ion intermediate is then attacked by

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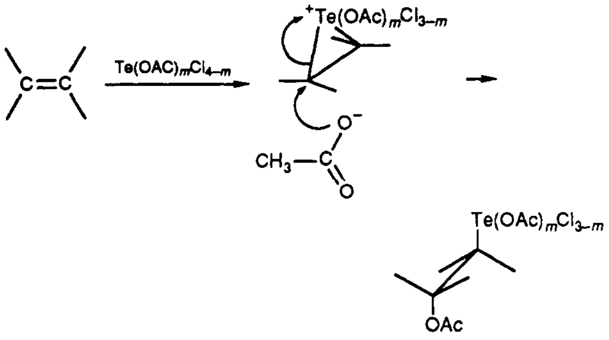
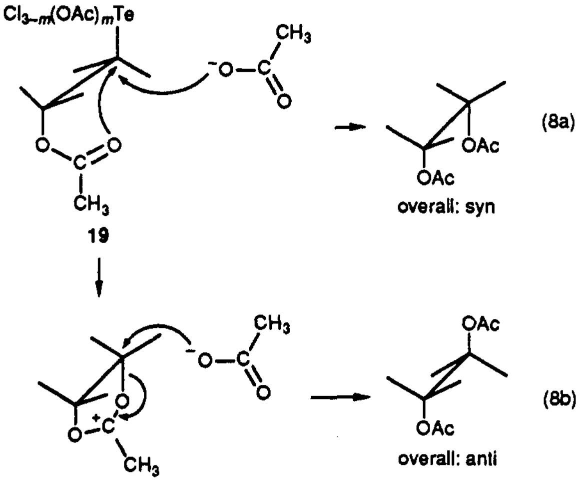
[12] Kambe, N.; Tsukamoto, T.; Miyoshi, N.; Murai, S.; Sonoda, N. *Chem. Lett.* **1987**, 269.

acetate (or acetic acid) to give anti addition in the formation of **19**.



19 (7)

Since the first step is cleanly anti, it is clear that stereospecificity is lost in the second step. This loss of stereospecificity, seen in the acetoxylation of (acetoxyalkyl)tellurium tribromides (eq 5 and Table VI), is consistent with a competition between rearward attack by acetate at the tellurium carbon and neighboring acetoxy participation in the oxidative cleavage reaction (eq 8).



After initial anti addition to give **19**, intermolecular attack by acetate causes inversion at the tellurium carbon and leads to an overall syn stereochemistry (eq 8a). Neighboring acetoxy participation leads to retention in the oxidative cleavage reaction and overall anti stereochemistry (eq 8b). Neighboring acetoxy assistance was previously suggested to account for the small amount of *trans*-1,2-diacetoxycyclohexane formed in the acetoxylation of *trans*-2-acetoxycyclohexylphenyl telluride.[12]

Stereochemical results for other 2-acetoxy tellurium compounds strongly suggest that competition between intermolecular attack by acetate and neighboring acetoxy participation accounts for the loss in stereospecificity in the second step of diacetoxylation. The almost planar nature of five-membered rings makes the conformation of *trans*-(2-acetoxycyclopentyl)tellurium tribromide ideal for neighboring acetoxy participation. This accounts for the large *retention* of stereochemistry in the acetoxylation of **14**. Acetoxylation of *trans*-(2-acetoxycyclohexyl)tellurium tribromide (**15**) gives mainly inversion of the tellurium carbon and overall syn stereochemistry. Neighboring acetoxy participation is less competitive than with **14** because the tellurium and acetoxy groups occupy equatorial positions in the preferred conformation of **15**. For the 2-acetoxy group to attack the tellurium carbon in the cyclohexyl system, the acetoxy must be in the energetically unfavorable axial position.

In acyclic systems, threo adduct **18a** undergoes less neighboring group participation than erythro adduct **18b**. The anti periplanar conformation needed for acetoxy participation in **18a** has an undesirable gauche interaction between the methyl groups (Chart I). This interaction is absent in the same conformation for **18b**. If we assume that the addition step is exclusively anti, this steric interaction results in a larger overall syn/anti ratio for **18a** (65/35) than for **18b** (46/54). Added acetate merely increases the rate of intermolecular attack. This explains the increase in the syn/anti ratio with added acetate.

A similar trend is observed for the diacetoxylation of *cis*- and *trans*-2-butene. There is less neighboring-group participation in the second step for *cis*-2-butene than for *trans*-2-butene because of the unfavorable methyl interaction, and the syn/anti ratio is higher (syn/anti: 92/8 vs 84/16). This trend was previously observed but unexplained for the diacetoxylation of *cis*-2-octene (syn/anti: 87/13) compared to that of *trans*-2-octene (syn/anti: 58/42) and for *cis*-4-octene (syn/anti: 89/11) compared to *trans*-4-octene (syn/anti: 56/44).[2]

Experimental Section

General Considerations. Melting points (uncorrected) were determined on a Mel-Temp melting point apparatus. ^{1}H and ^{13}C NMR spectra at 200 MHz were recorded on a Varian XL200E spectrometer, with a dual 5-mm switchable probe, as solutions in $CDCl_3$. ^{1}H and ^{13}C NMR spectra at 400 MHz were recorded on a Varian XL400 spectrometer. ^{125}Te NMR spectra were recorded on a Varian FT-80 spectrometer. Chemical shifts are reported in δ units downfield from TMS for carbon-13 and proton spectra and downfield from dimethyl telluride (neat) for tellurium-125 spectra. Assignment of carbon-13 resonances was aided by use of the APT (attached proton test) pulse sequence. Infrared spectra were obtained as solutions in chloroform with an IBM IR/44 Fourier transform infrared spectrometer. GLC analyses were carried out on a Perkin-Elmer 8410 gas chromatograph equipped with a 20-m SE-30 capillary column. Column chromatography was performed with J. T. Baker Chemical Co. silica gel (60–200 mesh). Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN.

Materials. Tellurium tetrachloride was prepared by the reaction of tellurium(IV) oxide (Alfa) and chlorotrimethylsilane (Aldrich) in chloroform-free ethanol and purified by sublimation.[13] Ammonium hexachlorotellurate was prepared as reported elsewhere.[14] Acetic acid was distilled prior to use. Anhydrous lithium acetate was obtained by drying the commercial dihydrate (Aldrich) at 200 °C under vacuum (1 mmHg). All alkenes and other organic compounds were commercially available and used without further purification.

Diacetoxylation of Cyclohexene with $TeCl_4$ and LiOAc in Acetic Acid. The typical procedure for the diacetoxylation of alkenes is as follows. A mixture of $TeCl_4$ (1.35 g, 5 mmol), LiOAc (1.32 g, 20 mmol), and acetic acid (15 mL) was stirred at 80–90 °C for 1 h, during which time the solution became homogeneous. To the resulting homogeneous solution was added cyclohexene (0.82 g, 10 mmol), and the solution was heated at 120 °C for 20 h. The solution was cooled, and precipitated black tellurium was filtered off. The filtrate was extracted with ether (50 mL) and the ether layer washed with water (2 × 50 mL). The aqueous layer was extracted again with ether (25 mL), and the ether layers were combined. The ethereal solution was washed with aqueous $NaHCO_3$, dried with $MgSO_4$, and evaporated to leave a yellow oil. This yellow oil was treated with acetic anhydride (1 mL) in pyridine (3 mL) to acylate any free hydroxy groups. The pyridine solution was diluted with ether (25 mL) and acidified with dilute HCl. The ethereal solution was dried with $MgSO_4$ and evaporated to give a yellow oil. The yellow oil was chromatographed on a short silica gel column (3.5 × 5 cm) with petroleum ether/ether (1:1). The ^{13}C NMR spectrum revealed

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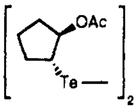
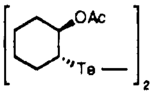
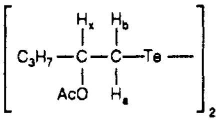
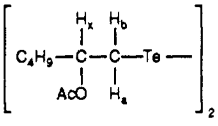
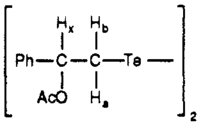
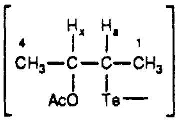
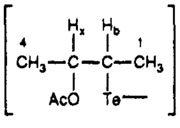
(13) Fukuzawa, S.; Irgolic, K. J.; O'Brien, D. H. *Heterocycl. Chem.* **1990**, *1*, 43.

(14) Brauer, G., Ed. *Handbook of Preparative Inorganic Chemistry*; Academic Press: New York, 1963; Vol. I, p 442.

Table IV. Spectral and Analytical Data for Bis(2-acetoxyalkyl) Ditellurides

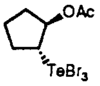
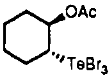
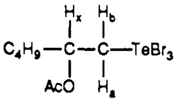
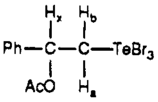
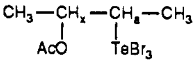
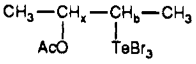
	^{1}H NMR		^{13}C NMR			IR	anal. found (calcd), %	
compd	group	δ (coupling, Hz)^a	group	δ	^{125}Te NMR, δ	($\nu_{C=O}$), cm^{-1}	C	H
	CH_2	1.5–1.8 (m), 1.9–2.2 (m)	CH_2	21.5,^{c} 30.7,^{c} 35.2^c		1730	33.05	4.43
	CH_3CO	2.01 (s)^c	$\mathit{C}\mathrm{H_3CO}$	20.9^c			(33.00)	(4.35)
	CH—Te	3.55–3.65 (m)	C—Te	23.2^c				
	CH—O	5.0–5.1 (m)	C—O	84.5^c				
7			C=O	170.1^c				
	CH_2	1.2–1.8 (m), 1.9–2.2 (m)	CH_2	24.03, 24.15	195.3	1729	35.35	4.93
	CH_3CO	2.07 (s)^b	CH_2	24.84, 24.92	204.2		(35.75)	(4.87)
	CH—Te	3.24 (dt, 4.0, 10.2)^b	CH_2	27.32, 27.41				
	CH—O	4.65 (dt, 4.3, 10.2)	CH_2	36.89, 37.20				
8	CH—O	4.70 (dt, 4.3, 10.2)	$\mathit{C}\mathrm{H_3CO}$	21.33, 21.36				
			C—Te	32.06, 32.18				
			C—O	77.54, 77.66				
			C=O	170.08, 170.12				
	CH_3, CH_2	0.93 (t), 1.36 (m), 1.64 (m)	CH_3	13.85^b		1730	32.92	5.21
	CH_3CO	2.06 (s)^b	CH_2	18.60,^{b} 36.90, 36.96			(32.74)	(5.10)
	CH_a—Te	3.388 (dd, 6.6, 12.1)	$\mathit{C}\mathrm{H_3CO}$	21.19^b				
	CH_a—Te	3.404 (dd, 6.6, 12.1)	C—Te	10.17, 10.32				
	CH_b—Te	3.494 (dd, 5.8, 12.1)^b	C—O	75.06, 75.11				
9	CH_x—O	4.894 (ddt, 5.8, 6.6, 6.2)	C=O	170.48^b				
	CH_x—O	4.901 (ddt, 5.8, 6.6, 6.2)						
	CH_3, CH_2	0.90 (t), 1.32 (m), 1.67 (m)	CH_3	13.94^b	106.2	1729	35.84	5.75
	CH_3CO	2.06 (s)^b	CH_2	22.46,^{b} 27.43^b	108.7		(35.84)	(5.58)
	CH_a—Te	3.388 (dd, 6.6, 12.1)	CH_2	34.48, 34.54				
	CH_a—Te	3.405 (dd, 6.6, 12.1)	$\mathit{C}\mathrm{H_3CO}$	21.18^b				
	CH_b—Te	3.495 (dd, 5.8, 12.1)^b	C—Te	10.17, 10.32				
10	CH_x—O	4.877 (ddt, 5.8, 6.6, 6.2)	C—O	75.26, 75.31				
	CH_x—O	4.883 (ddt, 5.8, 6.6, 6.2)	C=O	170.45^b				
	Ph	7.35 (bs)	Ph	126.6,^{b} 128.3^b	124.1	1730	41.90	4.09
	CH_3CO	2.044 (s), 2.047 (s)		128.5,^{b} 139.6^b	125.0		(41.30)	(3.81)
	CH_a—Te	3.518 (dd, 7.8, 12.0)	$\mathit{C}\mathrm{H_3CO}$	21.0^b				
	CH_a—Te	3.535 (dd, 7.6, 12.0)	C—Te	11.4, 11.5				
	CH_b—Te	3.565 (dd, 6.4, 12.0)	C—O	77.2^b				
11	CH_b—Te	3.573 (dd, 6.6, 12.0)	C=O	169.9^b				
	CH_x—O	5.820 (dd, 7.8, 64)						
	CH_x—O	5.843 (dd, 7.6, 6.6)						
$[(AcO)_2CHCH_2\text{-}Te\text{-}]_2$	CH_3CO	2.05 (s)	$\mathit{C}\mathrm{H_3CO}$	20.5		1765	26.25	3.28
12a	CH_2—Te	3.56 (d, 5.4)	O—C—O	91.3			(26.42)	(3.32)
			C—Te	6.7				
	O—CH—O	6.75 (t, 5.4)	C=O	168.4				
$[(AcO)_2CHCH_2]_2Te$	CH_3CO	2.06 (s)	$\mathit{C}\mathrm{H_3CO}$	20.5		1765	33.88	4.29
12b	CH_2—Te	2.99 (d, 5.4)	O—C—O	89.9			(34.49)	(4.34)
			C—Te	5.8				
	O—CH—O	6.82 (t, 5.4)	C=O	168.5				
	CH_3CO	1.853 (s), 1.855 (s)	$\mathit{C}\mathrm{H_3CO}$	21.0, 21.1	232.7	1729	30.05	4.65
	4-CH_3	1.132 (d, 6.3)^b	4-CH_3	18.0, 18.3	233.5		(29.69)	(4.57)
	1-CH_3	1.458 (d, 7.3), 1.462 (d, 7.3)	1-CH_3	23.7^c				
	CH_a—Te	3.347 (dq, 5.2, 7.3)	C—Te	22.2, 22.3				
	CH_a—Te	3.353 (dq, 5.2, 7.3)	C—O	75.7^c				
13a (threo)	CH_x—O	4.601 (dq, 5.2, 6.3)	C=O	170.0^c				
	CH_x—O	4.613 (dq, 5.2, 6.3)						
	CH_3CO	1.864 (s), 1.865 (s)	$\mathit{C}\mathrm{H_3CO}$	21.1^c	232.0	1729	29.97	4.56
	4-CH_3	1.110 (d, 6.3), 1.113 (d, 6.3)	4-CH_3	18.5^c	233.8		(29.69)	(4.57)
	1-CH_3	1.422 (d, 7.3), 1.425 (d, 7.3)	1-CH_3	23.3, 23.4				
	CH_b—Te	3.392 (dq, 5.2, 7.3)	C—Te	21.5, 21.6				
	CH_b—Te	3.405 (dq, 5.2, 7.3)	C—O	75.0, 75.1				
13b (erythro)	CH_x—O	4.636 (dq, 5.2, 6.3)	C=O	170.1^c				
	CH_x—O	4.641 (dq, 5.2, 6.3)						

[a] Coupling patterns: s = singlet; d = doublet; q = quartet; m = multiplet. [b] Resonances for each diastereomer not resolved at 400 MHz. [c] Resonances for each diastereomer not resolved at 200 MHz.

the presence of only the cis isomer of 3, *cis*-1,2-diacetoxycyclohexane, yield 0.70 g, 3.5 mmol (70%). The properties of diacetates 2–6 have been reported previously.[2]

Acetoxytellurination of Cyclohexene with $TeCl_4$ and LiOAc in Acetic Acid. The following example is a typical experimental procedure for the acetoxytellurination of alkenes. A mixture of $TeCl_4$ (2.70 g, 10 mmol), LiOAc (2.64 g, 40 mmol), and acetic acid (20 mL) was stirred at 80 °C for 1 h. To the resulting homogeneous solution was added $BF_3{\cdot}Et_2O$ (1.42 g, 10 mmol) and cyclohexene (1.64 g, 20 mmol) successively, and the mixture was heated at 80 °C for 3 h with stirring, during which time the solution became a dark gray suspension. The solution was poured into aqueous $Na_2S_2O_3$, and this mixture was extracted with ether (3 × 30 mL). The extract was dark orange to red. The ethereal solution was washed with aqueous $NaHCO_3$, dried with $MgSO_4$, and evaporated to leave dark red oil. The red oil was subjected to column chromatography on silica gel, with petroleum ether/ether (3:1) as eluent, to give *trans*-1,1-bis(2-accetoxycyclohexyl) ditelluride (8), yield 1.13 g, 2.1 mmol (42% based on $TeCl_4$). Spectral and analytical data for the bis(2-acetoxyalkyl)

Table V. Spectral and Analytical Data for (Acetoxyalkyl)tellurium Tribromides

compd	^{1}H NMR		^{13}C NMR		mp, °C	IR ($\nu_{C=O}$), cm^{-1}	anal. found (calcd), %	
	group	δ (coupling, Hz)[a]	group	δ			C	H
 **14**	CH_2	1.95 (m), 2.65 (m), 2.90 (m)	CH_2	21.1, 29.3, 30.3	91–93	1662	16.54	2.33
	CH_3CO	2.25 (s)	C—Te	68.4			(17.00)	(2.30)
	CH—Te	4.45 (q, 8.7)	C—O	79.1				
	CH—O	5.58 (q, 8.7)	CH_3CO	21.3, 179.1				
 **15**	CH_2	1.3–2.1 (m), 2.4–2.8 (m)	CH_2	23.0, 27.4, 28.4, 33.4	115–117	1648	18.88	2.71
	CH_3CO	2.31 (s)	C—Te	71.4			(18.89)	(2.57)
	CH—Te	4.41 (ddd, 4.9, 10.0, 12.6)	C—O	77.5				
	CH—O	5.20 (dt, 5.2, 10.0)	CH_3CO	22.0, 181.2				
 $C_4H_9-CH_x(OAc)-CH_aH_b-TeBr_3$ **16**	CH_3, CH_2	0.94 (t), 1.44 (m)	CH_3	13.8	95–97	1643	19.00	2.75
	CH_3CO	2.29 (s)	CH_2	22.2, 26.9, 34.4			(18.82)	(2.96)
	CH_b—Te	4.26 (dd, 1.7, 12.2)	C—Te	62.47				
	CH_a—Te	4.33 (dd, 10.3, 12.2)	C—O	76.25				
	CH_x—O	5.55 (ddt, 1.7, 10.3, 5.4)	CH_3CO	21.91, 181.34				
 $Ph-CH_x(OAc)-CH_aH_b-TeBr_3$ **17**	CH_3CO	2.36 (s)	Ph	126.4, 129.4, 129.8, 135.5	b	b	b	b
	CH_b—Te	4.39 (dd, 1.6, 12.2)	C—Te	63.4				
	CH_a—Te	4.60 (dd, 10.6, 12.2)	C—O	77.5				
	CH_x—O	6.56 (dd, 1.6, 10.6)	CH_3CO	22.1, 181.1				
	Ph	7.48 (s)						
 $CH_3-CH_x(OAc)-CH_a(TeBr_3)-CH_3$ **18a** (threo)	CH_3CO	2.28 (s)	CH_3	15.8, 19.6	>100 dec	1644	b	b
	CH_3	1.51 (d, 6.6), 2.26 (d, 7.2)	C—Te	69.7				
	CH_a—Te	4.41 (dq, 9.2, 7.2)	C—O	75.7				
	CH_x—O	5.43 (dq, 9.2, 6.6)	CH_3CO	22.0, 180.2				
 $CH_3-CH_x(OAc)-CH_b(TeBr_3)-CH_3$ **18b** (eyrthro)	CH_3CO	2.21 (s)	CH_3	11.6, 19.1	97–99	1655	14.32	2.30
	CH_3	1.51 (d, 6.8), 2.17 (d, 7.2)	C—Te	66.4			(14.94)	(2.30)
	CH_b—Te	4.26 (dq, 1.6, 7.2)	C—O	74.3				
	CH_x—O	5.90 (dq, 1.6, 6.7)	CH_3CO	21.8, 180.5				

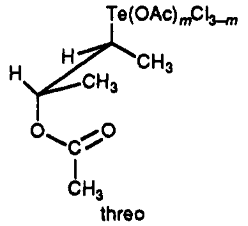
[a] Coupling patterns: s = singlet; d = doublet; t = triplet; q = quartet; m = multiplet. [b] Compound not stable long enough to permit analyses.

Table VI. Oxidative Cleavage of (2-Acetoxyalkyl)tellurium Tribromides[a]

entry no.	tribromide	product	isolated yield, %	isomer ratio[b]
1	14	2	77	cis/trans = 23/77
2[c]	14	2	88	cis/trans = 41/59
3	15	3	76	cis/trans = 77/23
4[c]	15	3	90	cis only
5	16	4	50	
6	17	5	0	
7[c]	17	5	90	
8	18a	6	87	meso/*dl* = 65/35
9[c]	18a	6	96	meso/*dl* = 89/11
10	18b	6	88	meso/*dl* = 54/46
11[c]	18b	6	75	meso/*dl* = 25/75

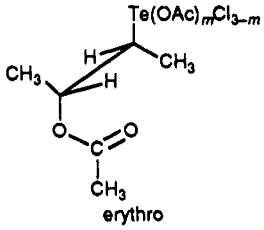
[a] Tribromide (2 mmol) and AcOH (10 mL) were reacted at 120 °C for 20 h. [b] Determined by ^{13}C NMR and GLC methods. [c] With LiOAc (10 mmol).

Chart I



threo

compd	overall stereochem	
	syn (meso)	anti (*dl*)
18a	65	35
18a + $^-$OAc	89	11
cis-2-butene (diacetoxylation)	92	8



erythro

compd	overall stereochem	
	syn (*dl*)	anti (meso)
18b	46	54
18b + $^-$OAc	75	25
trans-2-butene (diacetoxylation)	84	16

ditellurides 7–13 are summarized in Table IV.

Preparation of (2-Acetoxycyclohexyl)tellurium Tribromide. The following example is a typical experimental procedure for the preparation of (2-acetoxyalkyl)tellurium tribromides 14–18. In a 50-mL round-bottom flask containing a magnetic stirring bar was placed *trans*-1,1′-bis(2-acetoxycyclohexyl) ditelluride (9; 0.54 g, 1.1 mmol). Ethanol-free $CHCl_3$ (5 mL) was added to the flask, and the solution was cooled in a ice-water bath. Bromine (0.48 g, 3 mmol) in $CHCl_3$ (5 mL) was added dropwise to the solution with stirring. At the beginning of the reaction the solution turned reddish brown and then pale yellow. Evaporation of the solvent gave almost pure product, (2-acetoxycyclohexyl)tellurium tribromide (15), yield 1.01 g, 2.2 mmol (100%). Recrystallization from hexane/$CHCl_3$ gave yellow crystals, mp 115–117 °C. Spectral and analytical data for the (2-acetoxyalkyl)tellurium tribromides 14–18 are summarized in Table V. Compounds 17 and 18a were unstable at room temperature and decomposed into dark brown pastes and elemental tellurium in a few days. The other tribromides were stable enough to be kept even in the air for several months at room temperature.

Treatment of (2-Acetoxycyclohexyl)tellurium Tribromide (15) with LiOAc–Acetic Acid. The following example is a typical experimental procedure for the conversion of (2-acetoxyalkyl)tellurium tribromides into the corresponding *vic*-diacetates. A homogeneous mixture of (2-acetoxycyclohexyl)tellurium tribromide (15; 1.01 g, 2 mmol), LiOAc (0.66 g, 10 mmol), and acetic acid (10 mL) was stirred at reflux temperature for 20 h. The mixture was cooled, and the black precipitate of tellurium was filtered off. The filtrate was worked up in the same manner as for the diacetoxylation of cyclohexene. Evaporation of the solvent left an oily residue, which was chromatographed on a short silica gel column (3.5 × 5 cm) with petroleum ether/ether (1:1) to give *cis*-1,2-diacetoxycyclohexane (**3**), yield 0.36 g, 1.8 mmol (90%). ^{13}C NMR spectroscopy showed the presence of only the cis isomer of **3**. When the reaction was carried out in the absence of LiOAc, ^{13}C NMR spectroscopy showed that the product was a mixture of cis and trans isomers of **3** in the ratio 77:23.

Acknowledgment. Financial support by the Robert A. Welch Foundation of Houston, TX, and the Board of Regents of the Texas A&M University System is gratefully acknowledged.

Synthesis and Study of the Benzyl- and Naphthylpalladium(IV) Complexes $PdBrMe_2(CH_2Ar)(L_2)$ (L_2 = bpy, phen) and μ-Hydrocarbyl Palladium(IV)–Palladium(IV) and Palladium(IV)–Platinum(IV) Complexes and the Structure of *fac*-$PdBrMe_2(CH_2\text{-}p\text{-}C_6H_4Br)(phen)$

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Received June 8, 1990

Benzyl and naphthyl bromides react with dimethylpalladium(II) complexes $PdMe_2(L_2)$ (L_2 = bpy, phen) to form the palladium(IV) complexes $PdBrMe_2(CH_2Ar)(L_2)$ (Ar = p-C_6H_4X (X = H, Me, Br, NO_2), C_6F_5) and $PdBrMe_2(CH_2Ar)(bpy)$ (Ar = 1-$C_{10}H_7$, 2-$C_{10}H_7$). The 2,2′-bipyridyl complexes and $PdBrMe_2(CH_2C_6F_5)(phen)$ reductively eliminate ethane with formation of $PdBr(CH_2Ar)(bpy)$ and $PdBr(CH_2C_6F_5)(phen)$, respectively, on warming to ca. 40 °C in $(CD_3)_2CO$. The other 1,10-phenanthroline complexes undergo less selective reductive elimination, to form $PdBr(CH_2Ar)(phen)$ and $PdBrMe(phen)$ in a ca. 10:1 ratio (Ar = p-C_6H_4Me) and ca 3:1 ratio (Ar = p-C_6H_4X where X = H, Br, NO_2). α,α'-Dibromo-m-xylene reacts with $PdMe_2(bpy)$ to form $PdBrMe_2(CH_2\text{-}m\text{-}C_6H_4CH_2Br)(bpy)$, and this complex undergoes further oxidative addition with $MMe_2(bpy)$ (M = Pd, Pt) to form the binuclear complexes $(PdBrMe_2(bpy))_2(\mu\text{-}m\text{-}(CH_2)_2C_6H_4)$ and $(PdBrMe_2(bpy))(PtBrMe_2(bpy))(\mu\text{-}m\text{-}(CH_2)_2C_6H_4)$. The complex $PdBrMe_2(CH_2\text{-}p\text{-}C_6H_4Br)(phen)$ has a *fac*-PdC_3 configuration with the Pd–Br bond (2.636 (1) Å) trans to the benzyl group. The Pd–C(benzyl) bond (2.091 (6) Å) is ca. 0.06 Å longer than the Pd–CH_3 bonds. Crystals of $PdBrMe_2(CH_2\text{-}p\text{-}C_6H_4Br)(phen)$ are monoclinic, space group $P2_1/n$, with a = 8.465 (2) Å, b = 9.051 (2) Å, c = 26.364 (6) Å, β = 96.75 (2)°, and Z = 4.

Introduction

Although organoplatinum(IV) compounds have been known since 1907,[2] and (pentafluorophenyl)palladium(IV) complexes were isolated in 1975,[3] the first detailed studies implicating the formation of (hydrocarbyl)palladium(IV) species were reported by Stille and co-workers in 1976–1981[4-10] and by Baird and co-workers in 1982.[11] Gillie and Stille reported that *trans*-$PdMe_2$(TRANSPHOS) (TRANSPHOS = 2,11-bis((diphenylphosphino)methyl)benzo[*c*]phenanthrene) is stable toward reductive elimination at 100 °C in $(CD_3)_2SO$ but that addition of CD_3I to the complex results in the formation of CD_3CH_3 at ambient temperature.[7] These results suggest the occurrence of an oxidative-addition–reductive-elimination sequence, presumably via formation of the palladium(IV) cation $[PdMe_2(CD_3)(TRANSPHOS)]^+$, since the orientation of the diphosphine ligand prevents iodide coordination to form the octahedral geometry expected for d^6 palladium(IV).[7] Kinetic studies by Moravskiy and Stille are consistent with occurrence of the S_N2 mechanism for oxidative addition of methyl iodide to *cis*-dimethylpalladium(II) phosphine complexes to form palladium(IV) intermediates, e.g. "$PdIMe_3(PMePh_2)_2$", followed by rapid reductive elimination of ethane to form methyliodopalladium(II) products.[9] Related studies by Milstein and Stille also suggest the transient formation of similar benzylpalladium(IV) complexes,[5,6] e.g. formation of "$PdBrMe_2(CH_2Ph)(PPh_3)_2$" followed by reductive elimination to form ethylbenzene and *trans*-$PdBrMe(PPh_3)_2$, with inversion at carbon observed in the analogous reaction sequence by use of optically active α-deuteriobenzyl bromide.[5,10] In 1982 Weinberg, Hunter, and Baird reported that the reaction of iodomethane with $(PdCH_2CH(CO_2Et)_2CH_2NMe_2(\mu\text{-}Cl))_2$ in $CDCl_3$ gave a ^1H NMR spectrum exhibiting a singlet at 2.20 ppm, tentatively

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