

TELLURIUM IN ORGANIC SYNTHESIS

V *. X-RAY STRUCTURE OF 8-ETHOXY-4-CYCLOOCTENYLTELLURIUM TRICHLORIDE AND ITS RELEVANCE TO THE TeO_2 -OXIDATION OF ALKENES

J. BERGMAN and L. ENGMAN

Department of Organic Chemistry, Royal Institute of Technology, S-100 44 Stockholm (Sweden)

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Summary

The molecular structure of 8-ethoxy-4-cyclooctenyltellurium trichloride has been determined from three-dimensional X-ray diffraction data. The crystal belongs to the monoclinic system, space group $P2_1/n$, with four formula units in a cell of dimensions: a 7.712(1), b 13.406(3), c 13.820(2) Å and β 95.18(1)°. The structure was solved by the conventional heavy atom method, and refined by the least-squares procedure to $R = 0.025$ for 2199 reflections.

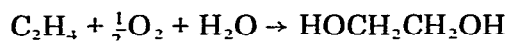
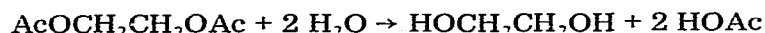
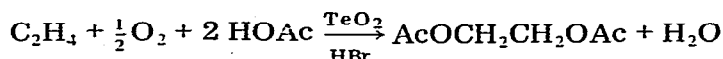
The compound is formed from the corresponding β -chloroalkyltellurium trichloride, obtained from TeCl_4 and *cis*, *cis*-1,5-cyclooctadiene, by an unusually mild solvolytic substitution reaction in ethanol. Similar β -chloroalkyltellurium compounds are postulated as intermediates in the TeO_2 oxidation of alkenes to alkanediol diacetates and alkanediol monoacetates in HOAc containing a lithium halide, LiX. Oxidation of *cis*-2-butene and *trans*-2-butene with $\text{TeO}_2/\text{HOAc}/\text{LiBr}$ gave a high preference for *cis*-stereochemistry in the products while 1-decene showed no stereospecificity.

Introduction

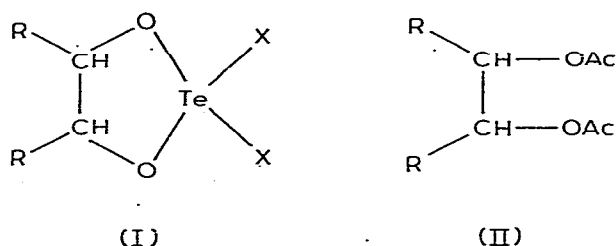
Catalytic systems containing TeO_2 and HOAc have attracted considerable attention [1,2] in recent years. Ethylene, for example, can be catalytically con-

* For part 4, see ref. 23.

verted into ethyleneglycol in high yields (95%):

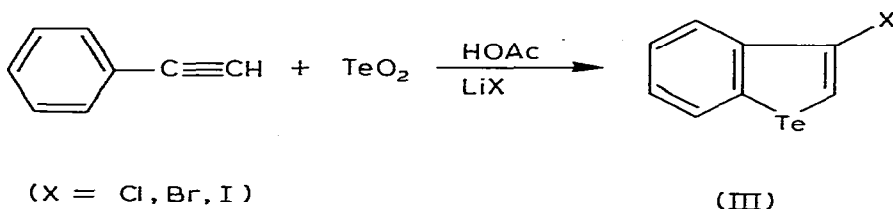


Although this process is used commercially for production of ethyleneglycol (Oxirane in Texas, USA) no mechanistic study has been published so far. One of the early patents [3] suggested a cyclic intermediate I, which would undergo solvolysis to the corresponding diacetate II.

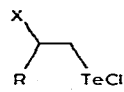


If the cyclic tellurium ester I is the actual intermediate in the oxidation of alkenes, this would give rise to a strong preference for *cis*-stereochemistry of the diacetates II, by analogy with the MnO_4^- and OsO_4 oxidations of alkenes. However, we did not find any such preference with the alkenes examined.

A further indication that a different mechanism may operate, appeared in the reaction of phenylacetylene with the system $\text{TeO}_2/\text{HOAc}/\text{LiX}$ [4]:



The introduction of a halogen atom at the triple bond was apparently a result of an electrophilic attack by a hitherto unknown species formed from TeO_2 and LiX . The addition product subsequently cyclizes to give, after a reductive elimination, the benzo [b] tellurophene derivative III. It seems reasonable that a similar electrophilic attack may occur in the first step of the oxidation of alkenes with TeO_2 , and it therefore appeared to be of interest to study well-defined com-

pounds of the type , where X is a halogen atom or an oxygen-bearing substituent.

To our knowledge only one well-defined compound of this kind is described in the literature, viz. 2-chloropropyltellurium trichloride [5], the 1/1 addition product from TeCl_4 and propene. However, attempts to repeat this experiment

resulted in mixtures of products, and we therefore decided to look for other β -chloroalkyltellurium trichlorides which could be easily prepared from alkenes and TeCl_4 .

Results and discussion

SeO_2 oxidations of alkenes in HOAc with mineral acid catalysis are well-known and give mixtures of alkanediol diacetates and alkanediol monoacetates [6,7]. Substrates such as *cis*- and *trans*-2-butene show a high preference for *cis*-stereochemistry in the products. Oxidation of cyclohexene [7] is less specific. The results of TeO_2 oxidation of the above-mentioned butenes are presented in Table 1. Oxidations were carried out in HOAc in the presence of LiBr, and both 2,3-butanediol diacetates and 2,3-butanediol monoacetates were formed. The stereochemical results are very much alike those obtained with SeO_2 in the presence of a mineral acid. An overall *cis*-addition is preferred. The same stereochemistry is present in the diacetates and the monoacetates.

Oxidation of 1-decene with $\text{TeO}_2/\text{HOAc}/\text{LiBr}$ gave almost pure 1,2-decanediol diacetate in good yield (87%). *Z*-1-Deuterio-1-decene [9] yielded equal amounts of the *erythro*- and the *threo*-form as revealed by the ^1H NMR spectrum [10]. The oxidations of alkenes with TeO_2 seems to give varying amounts of diol monoacetates as well as varying stereospecificity depending on the substrate. It was recently shown [8] that benzeneseleninic acid reacts with olefins in acetic acid to give 2-acetoxyalkylphenyl selenides in good yields. This reaction seems to have much in common with the addition of TeO_2 to phenylacetylenes and also to our postulated first step of the TeO_2 oxidation of alkenes, except that the acetate group is replaced by a halogen atom.

In order to further study the reactions of β -chloroalkyltellurium trichlorides, we synthesized the 1/1 adduct from *cis*, *cis*-1,5-cyclooctadiene and TeCl_4 (IV). This compound was obtained in good yield (64%) by mixing the two reactants in dry ethanol-free chloroform at 0°C . A possible bicyclic structure V could be excluded from the proton-decoupled ^{13}C NMR spectrum which showed eight different peaks.

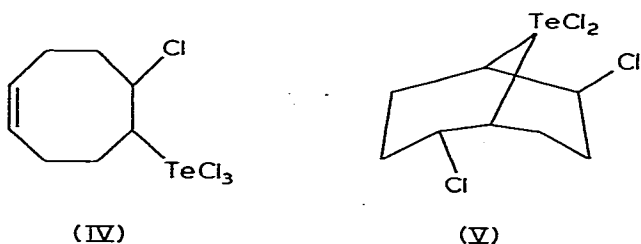
Compound IV is unstable in air at room temperature and slowly decomposes into a black tar. At -15°C it can be stored for several months. A few hours reflux of IV in ethanol, or even a recrystallization, yielded in good yield (76%) a highly crystalline compound in which a chlorine atom had been replaced by an ethoxy

TABLE 1
OXIDATION OF 2-BUTENES

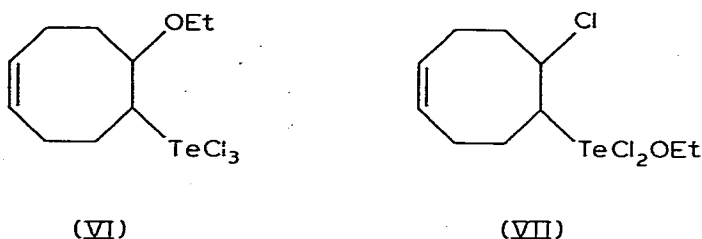
Substrate	2,3-Butanediol diacetate (%) ^a	<i>meso</i> / <i>d,l</i> -ratio	2,3-Butanediol monoacetate (%) ^a	<i>meso</i> / <i>d,l</i> -ratio ^b
<i>cis</i> -2-Butene	19.3	89/11	16.0	91/9
<i>trans</i> -2-Butene	9.2	35/65	21.1	33/67

^a Isolated yield. ^b Monoacetates were converted to diacetates with acetic anhydride and determined by GLC.

group as revealed by ^1H NMR and mass spectral data. However, a choice could

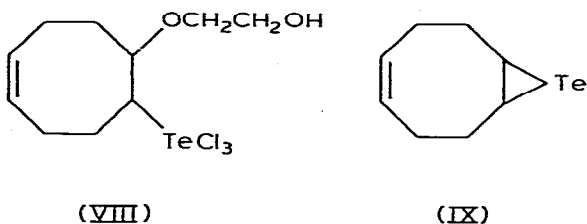


not be made between structures VI and VII. We therefore undertook an X-ray



crystallographic study which gave conclusive evidence for structure VI, with a *trans*-orientation of the TeCl_3 and the ethoxy group. The β -halogen atom of IV seems to be extremely sensitive to nucleophilic attack, probably because of some sort of neighbouring group participation. A similar mechanism has been suggested for the solvolysis of 2-halocyclohexyl selenocyanate, which gave complete retention of configuration at the β -carbon [12]. Treatment of IV with ethylene glycol rapidly yielded a crystalline compound assigned structure VIII from spectroscopic data.

Reduction of IV with aqueous $\text{Na}_2\text{S}_2\text{O}_5$ caused separation of elemental tellurium and regeneration of *cis*, *cis*-1,5-cyclooctadiene. The epitelluride IX is a possible intermediate in this reaction. Epitellurides have previously been postulated as intermediates in the conversion of epoxides into alkenes by sodium *O,O*-diethyl phosphorotelluroate [13].



Structure analysis

The composition of compound VI, subjected to an X-ray analysis, was known from elemental analysis to be $\text{C}_{10}\text{H}_{17}\text{Cl}_3\text{OTe}$. Suitable crystals were obtained by recrystallisation from acetonitrile.

The intensity data were collected at $25 \pm 2^\circ\text{C}$ by a computer controlled four-

TABLE 2
CRYSTAL DATA

Mol. formula: $\text{C}_{10}\text{H}_{17}\text{Cl}_3\text{OTe}$	Habit: Prismatic a
Formula weight: 388.41	Crystal size: $0.28 \times 0.23 \times 0.23$
Melting point: $138-140^\circ\text{C}$	Systematic absences:
Unit Cell: Monoclinic	$h\ 0\ l$ for $h + l \neq 2n$
Cell parameters:	$0\ k\ 0$ for $k \neq 2n$
a 7.712(1) Å	Space group: $P2_1/n$
b 13.406(3) Å	General positions:
c 13.820(2) Å	x, y, z
β 95.18 (1) $^\circ$	$\bar{x}, \bar{y}, \bar{z}$
$V = 1423\ \text{\AA}^3$	$\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$
$Z = 4$	$-\frac{1}{2} + x, -\frac{1}{2} - y, -\frac{1}{2} + z$
D_x 1.81 g cm $^{-3}$	Radiation: Mo- K_α
D_m 1.80 g cm $^{-3}$ a	λ : 0.71069 Å
	$\mu(\text{Mo-}K_\alpha)$ 27.0 cm $^{-1}$

a By flotation in carbon tetrachloride/methyl iodide at 25°C .

circle diffractometer of type Syntex P2₁, equipped with a scintillation counter. The crystallographic data are summarized in Table 2.

X-ray data collection. Approximate positions of about 20 reflections were obtained from an oscillation photograph on the diffractometer. These data were used for an automatic determination of the lattice constants. More precise values for the unit cell dimensions were determined from 22 strong reflections with high 2θ -values, and refined using least squares methods. The ω -scan mode was used for the intensity data collection with variable scan speeds, the minimum scan speed being $0.49^\circ\text{ min}^{-1}$. Methods for background measurements and intensity calculations are described elsewhere [14].

After every 100th reflection the intensities of four check reflections were measured. Their intensities varied within $\pm 5\%$ during data collection without any trend.

A semi-empirical absorption correction method was used [16]. The intensities of 11 selected reflections, with 2θ values evenly distributed over the 2θ range used, were measured for a full flat-cone rotation around the diffraction vector in steps of 10° . The relative intensity variations obtained were used to correct the intensities of all measured reflections in appropriate 2θ intervals. The largest measured relative reduction in intensity was from 1.00 to 0.82.

All intensities were corrected for Lorenz and polarization effects and approximate values for scaling and temperature factors were calculated using a Wilson plot. Of the 2500 possible independent reflections for $2\theta < 50^\circ$ 301 had intensities less than $1.96\ \sigma(I)$ and were given zero weight in the following least-squares refinement.

Structure determination and refinements

The structure was solved by the heavy-atom technique. From a three-dimensional Patterson function the tellurium atoms could be identified as occupying the fourfold general position of the space group $P2_1/n$. With the use of the posi-

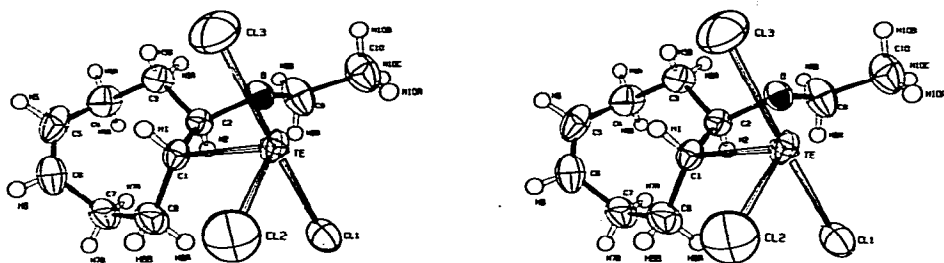


Fig. 1. Stereoscopic view of the molecule as represented by thermal vibration ellipsoids.

tional parameters for the Te atoms, derived from the Patterson function, a three-dimensional electron density map was calculated. The remaining non-hydrogen atoms were easily located. Full-matrix least-squares refinement with individual anisotropic temperature factors for all atoms led to a conventional R index ($\sum \|F_o| - |F_c| \| / |F_o|$) of 0.034. The 17 hydrogen atoms were then located in a new difference map. They were selected from the 25 highest peaks, partly by geometrical reasons.

With all atoms included the refinement was continued until all 204 parameter values showed shifts in the last cycle, less than 1% of the corresponding standard deviations. With all nonhydrogen atoms anisotropic and with the hydrogens isotropic the final R -value was $R = 0.025$ ($R_w = 0.034$) * for 2199 observed reflections. Including data with zero weight $R = 0.032$ ($R_w = 0.037$) for 2500 reflections.

The least squares refinements were based on minimization of $\sum w_i \|F_o| - |F_c|^2$. The weighting scheme used was $w(s) = 1/(\sigma^2(F_o) + (0.03 F_o)^2)$ with a cut-off limit of $F_o > 3.92 \sigma(F_o)$. The goodness-of-fit $(\sum (F_o - F_c)^2 / (m-s))^{1/2}$, where m is the number of reflections used and s is the number of parameters) is 1.0. Struc-

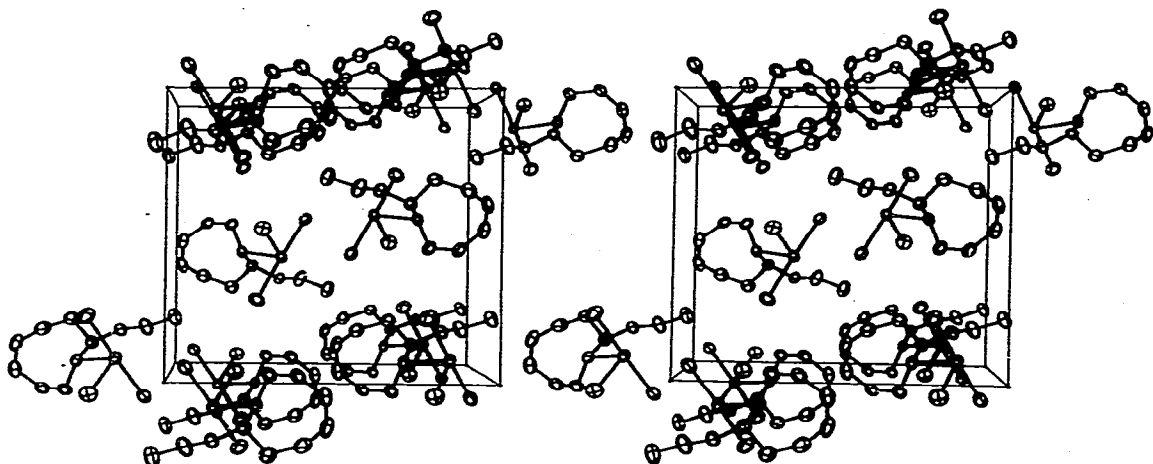


Fig. 2. Stereoscopic view of the unit cell as represented by thermal vibration ellipsoids.

* R_w is a weighted R value defined as

$$R_w = (\sum w_i \|F_o| - |F_c|^2 / \sum w_i |F_o|^2)^{1/2}$$

TABLE 3

FINAL FRACTIONAL ATOMIC POSITIONAL PARAMETERS WITH ESTIMATED STANDARD DEVIATIONS IN PARANTHESES

Atom	X	Y	Z
Te	0.02916(3)	0.07988(2)	0.85273(1)
Cl(1)	0.30867(15)	0.43550(7)	0.56750(6)
Cl(2)	-0.19903(14)	-0.02507(9)	0.79028(8)
Cl(3)	-0.11311(15)	0.22895(8)	0.77438(7)
O	0.30701(28)	0.16333(17)	0.85143(15)
C(1)	0.17327(44)	0.06356(24)	0.72574(22)
C(2)	0.34193(43)	0.11681(25)	0.75988(22)
C(3)	0.39484(57)	0.19767(30)	0.69075(29)
C(4)	0.45974(66)	0.15970(38)	0.59530(34)
C(5)	0.32687(61)	0.11462(39)	0.52424(28)
C(6)	0.26601(60)	0.02360(41)	0.52785(28)
C(7)	0.31441(65)	-0.04765(34)	0.60814(30)
C(8)	0.19164(68)	-0.04308(33)	0.68961(31)
C(9)	0.45418(55)	0.16691(45)	0.92356(31)
C(10)	0.39961(79)	0.20482(49)	1.01613(34)
H(1)	0.1002(43)	0.1032(23)	0.6812(22)
H(2)	0.4374(51)	0.0700(23)	0.7742(24)
H(3A)	0.4963(52)	0.2367(27)	0.7302(26)
H(3B)	0.2954(51)	0.2408(27)	0.6788(25)
H(4A)	0.5206(80)	0.2280(45)	0.5728(41)
H(4B)	0.5409(62)	0.1137(36)	0.6122(30)
H(5)	0.2850(51)	0.1546(29)	0.4726(28)
H(6)	0.1842(59)	0.0000(34)	0.4829(32)
H(7A)	0.4356(68)	-0.0326(41)	0.6341(30)
H(7B)	0.3168(69)	-0.1082(38)	0.5808(38)
H(8A)	0.2297(66)	-0.0872(32)	0.7384(37)
H(8B)	0.0793(67)	-0.0690(30)	0.6689(30)
H(9A)	0.5017(85)	0.0934(40)	0.9273(40)
H(9B)	0.5588(74)	0.2009(41)	0.9020(38)
H(10A)	0.3212(84)	0.1667(48)	1.0376(41)
H(10B)	0.3551(68)	0.2776(41)	0.9982(35)
H(10C)	0.4790(102)	0.1992(55)	1.0621(52)

ture factors can be obtained from the authors on request.

A stereoscopic view of the molecule with the thermal vibration ellipsoids is given in Fig. 1. A view of the unit cell is given in Fig. 2. Positional and thermal parameters are listed in Tables 3 and 4.

Discussion of the structure

The intramolecular bond lengths and bond angles of the molecule are given in Table 5. The bond lengths and angles around the tellurium atom are in good agreement with other investigations of similar tellurium(IV) compounds [17]. From the literature it is known that tellurium can have the coordination numbers 4 [18], 5 [5] or 6 [19] in chloro compounds. In the investigated 8-ethoxy-4-cyclooctenyltellurium trichloride, the tellurium atom has 6 neighbours in space. Four of these atoms (C(1), Cl(1), Cl(2) and Cl(3)) have normal bonding distances. The fifth is the oxygen atom of the ethoxy group which occurs at a distance of 2.419(2) Å from the Te atom. (A normal bonding Te—O—distance is 1.90 Å) [21].

TABLE 4
FINAL ISOTROPIC (HYDROGEN ATOMS) AND ANISOTROPIC THERMAL PARAMETERS ($\text{\AA}^2$) WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES. The expression used is: $\exp -4(B_{11}h^2 + \dots + 2B_{12}hka + \dots)$.

Atom	B	Atom	B ₁₁	B ₂₂	B ₃₃	B ₁₂	B ₁₃	B ₂₃
H(1)	2.2(6)	Te	2.74(1)	3.39(1)	2.29(1)	0.35	0.69(0)	0.32(0)
H(2)	2.7(7)	Cl(1)	5.67(5)	4.44(4)	3.27(3)	-1.49(3)	0.72(3)	-0.94(3)
H(3A)	3.5(7)	Cl(2)	3.66(4)	6.05(5)	5.62(4)	-1.35(4)	0.72(3)	-0.14(4)
H(3B)	3.5(7)	Cl(3)	5.43(5)	5.01(4)	5.04(4)	2.13(4)	0.83(3)	1.22(3)
H(4A)	8.4(14)	O	2.64(9)	3.76(10)	2.90(9)	0.19(7)	0.35(7)	-0.47(7)
H(4B)	4.7(9)	C(1)	2.83(13)	3.56(14)	2.19(11)	0.23(10)	0.97(10)	0.29(10)
H(5)	3.8(7)	C(2)	2.60(12)	3.26(13)	2.86(12)	0.50(11)	0.70(10)	-0.04(10)
H(6)	4.9(10)	C(3)	4.16(18)	3.93(17)	4.32(17)	-0.49(15)	1.69(14)	0.04(14)
H(7A)	5.9(11)	C(4)	5.48(23)	4.90(21)	5.03(21)	-0.19(19)	2.94(18)	0.50(17)
H(7B)	6.8(12)	C(5)	5.37(21)	6.60(24)	2.78(15)	1.82(19)	1.59(14)	1.31(16)
H(8A)	5.0(10)	C(6)	4.40(19)	7.35(27)	2.68(14)	0.23(18)	1.13(13)	-0.80(16)
H(8B)	4.7(10)	C(7)	5.62(23)	4.21(18)	3.84(16)	-0.06(16)	1.43(15)	-1.19(14)
H(9A)	7.3(14)	C(8)	5.60(22)	3.99(17)	3.72(17)	-0.68(17)	1.85(15)	-0.99(14)
H(9B)	7.3(13)	C(9)	3.29(17)	7.96(29)	3.97(18)	0.24(18)	-0.39(14)	-1.91(18)
H(10A)	8.1(18)	C(10)	5.37(26)	7.20(31)	3.67(18)	0.90(23)	-0.57(18)	-1.18(18)
H(10B)	6.8(12)							
H(10C)	10.8(21)							

TABLE 5

INTRAMOLECULAR BOND LENGTHS AND ANGLES WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

Te-Cl(1)	2.505(1)	C(2)-H(2)	0.974(36)	Cl(1)-Te-Cl(2)	91.51(4)	H(3B)-C(3)-C(4)	111.6(22)
Te-Cl(2)	2.355(1)	C(3)-H(3A)	1.053(38)	Cl(1)-Te-Cl(3)	176.24(4)	H(4A)-C(4)-H(4B)	110.1(43)
Te-Cl(3)	2.481(1)	C(3)-H(3B)	0.963(29)	Cl(1)-Te-Cl(1)	90.36(9)	H(4A)-C(4)-C(3)	98.5(32)
Te-C(1)	2.172(3)	C(4)-H(4A)	1.087(61)	Cl(2)-Te-Cl(3)	92.00(4)	H(4A)-C(4)-C(5)	116.4(32)
C(1)-C(2)	1.521(5)	C(4)-H(4B)	0.894(48)	Cl(2)-Te-Cl(1)	93.65(9)	H(4B)-C(4)-C(3)	106.1(30)
C(2)-C(3)	1.525(5)	C(5)-H(5)	0.927(40)	Cl(3)-Te-Cl(1)	88.10(9)	H(4B)-C(4)-C(5)	108.5(30)
C(3)-C(4)	1.539(6)	C(6)-H(6)	0.901(45)	Te-C(1)-C(2)	100.83(20)	H(5)-C(5)-C(4)	116.3(24)
C(4)-C(5)	1.483(7)	C(7)-H(7A)	0.992(52)	Te-C(1)-C(8)	115.37(25)	H(5)-C(5)-C(6)	117.9(24)
C(5)-C(6)	1.310(7)	C(7)-H(7B)	0.897(52)	C(2)-C(1)-C(8)	116.07(30)	H(6)-C(6)-C(5)	122.0(29)
C(6)-C(7)	1.486(6)	C(8)-H(8A)	0.925(48)	C(2)-C(1)-C(3)	114.15(29)	H(6)-C(6)-C(7)	113.7(29)
C(7)-C(8)	1.536(7)	C(8)-H(8B)	0.953(50)	C(1)-C(2)-O	104.49(25)	H(7A)-C(7)-H(7B)	106.3(44)
C(8)-C(1)	1.525(5)	C(9)-H(9A)	1.051(56)	O-C(2)-C(3)	108.71(27)	H(7A)-C(7)-C(6)	107.7(29)
C(9)-C(10)	1.473(7)	C(9)-H(9B)	0.996(57)	C(2)-C(3)-C(4)	115.35(34)	H(7A)-C(7)-C(8)	110.4(29)
C(2)-O	1.457(4)	C(10)-H(10A)	0.864(65)	C(3)-C(4)-C(5)	116.34(40)	H(7B)-C(7)-C(6)	106.3(34)
C(9)-O	1.442(5)	C(10)-H(10B)	1.056(55)	C(4)-C(5)-C(6)	125.66(44)	H(7B)-C(7)-C(8)	112.4(34)
C(1)-H(1)	0.957(32)	C(10)-H(10C)	0.846(76)	C(5)-C(6)-C(7)	124.09(43)	H(8A)-C(8)-H(8B)	101.8(40)
				C(6)-C(7)-C(8)	113.07(38)	H(8A)-C(8)-C(7)	109.4(30)
				C(7)-C(8)-C(1)	111.03(36)	H(8A)-C(8)-C(1)	113.1(30)
				C(2)-O-C(9)	114.76(28)	H(8B)-C(8)-C(7)	111.7(27)
				O-C(9)-C(10)	110.06(40)	H(8B)-C(8)-C(1)	109.3(27)
				H(1)-C(1)-Te	98.5(19)	H(9A)-C(9)-H(9B)	98.9(45)
				H(1)-C(1)-C(2)	112.0(19)	H(9A)-C(9)-O	104.6(32)
				H(1)-C(1)-C(8)	112.1(19)	H(9A)-C(9)-C(10)	113.9(32)
				H(2)-C(2)-O	107.0(20)	H(9B)-C(9)-O	114.6(32)
				H(2)-C(2)-C(1)	111.7(20)	H(9B)-C(9)-C(10)	113.8(32)
				H(2)-C(2)-C(3)	110.2(20)	H(10A)-C(10)-H(10B)	113.7(50)
				H(3A)-C(3)-H(3B)	109.3(30)	H(10A)-C(10)-H(10C)	99.8(66)
				H(3A)-C(3)-C(2)	104.9(20)	H(10A)-C(10)-C(9)	111.0(42)
				H(3A)-C(3)-C(4)	108.9(20)	H(10B)-C(10)-C(1)	117.1(59)
				H(3B)-C(3)-C(2)	106.2(22)	H(10B)-C(10)-C(9)	103.2(29)
						H(10C)-C(10)-C(9)	112.2(51)

The bonding about tellurium in the free molecule might be considered to be square pyramidal with O, Cl(1), Cl(2), and Cl(3) in the base, C(1) at the apex, and the lone-pair of electrons probably occupying the sixth position of an octahedron around tellurium. The basal plane is somewhat distorted with the O—Te—Cl angle being only $61.45(10)^\circ$. This could be explained by ring-strain in the four-membered ring formed by Te, O, C(1), and C(2). As a result of coordination the angle O—C(2)—C(1) is as small as $104.49(25)^\circ$.

The sixth close neighbour is a chlorine atom (Cl(1)) which originates from another molecule. This very weakly bonded chlorine atom occurs at a distance of $3.558(1)$ Å from the Te atom and is oriented in the same direction as the lone electron pair (intermolecular angles: Cl(2)—Te—Cl(1) $82.73(3)^\circ$, Cl(1)—Te—Cl(1) = $81.10(3)^\circ$). It is thus completing a distorted octahedral configuration about tellurium in the crystalline solid. The structure can be considered as being built up of dimers with the TeCl_3 -groups pointing towards one other, donating one of the chlorine atoms. The interaction between the lone electron pair and the chlorine atom is probably due to electron delocalization from Cl to tellurium-(IV). Similar delocalization seems to be present also in β -dimethyltellurium diiodide [22]. However, in this compound the effect is larger, as judged by the difference between the Te...I and Te...Cl distances which is 0.1 Å shorter than the difference in ionic radius between I^- and Cl^- .

Data program

The program system supplied by Syntex (XTL version 2 [15]) for a NOVA 32K computer with a disk memory unit, was used for the calculations. In addition the thermal-ellipsoid plot program for crystal structure illustrations, ORTEP 2 was used [20].

Concluding remarks

Our hypothesis, that the first step in TeO_2 oxidations of alkenes is an electrophilic *trans*- addition, originated from the results obtained in oxidations of phenylacetylenes, where the postulated intermediate is trapped by an internal cyclization. The remarkable ease of substitution of the β -halogen atom, as exemplified by the 1/1 adduct of *cis*, *cis*-1,5-cyclooctadiene and TeCl_4 , seems to explain satisfactorily the introduction of the first acetoxy group into the final diol diacetate or diol monoacetate (although we could not isolate any well-defined product upon acetolysis of IV). Introduction of a second acetoxy group or a hydroxy group may involve a nucleophilic displacement of a tellurium compound, and much work remains to be done to elucidate the nature of this reaction. 1,2 metal oxygen shift has been postulated in the oxidative cleavage of alkylphenyl tellurides and selenides [11]. A similar mechanism may well operate if one of the original TeO_2 oxygens still remains on the Te atoms at this stage of the reaction.

Experimental

Materials

cis-2-Butene, *trans*-2-butene, 1-decene and *cis*, *cis*-1,5-cyclooctadiene were obtained from Fluka. TeCl_4 was a Merck product. *Z*-1-Deuterio-1-decene was pre-

pared as described in the literature [9]. Chloroform was shaken several times with water and dried over CaCl_2 .

Analysis and spectroscopic measurements

Elemental analysis was performed by Centrala Analyslaboratoriet, Uppsala Sweden. NMR spectra were recorded on a Bruker WP 200 instrument. Infrared spectra were obtained using a Perkin-Elmer 257 instrument. Mass spectra were obtained with an LKB 9000 mass spectrometer. For the GLC analysis a glass column containing 2% OV 17 on AW-DMCS Chromosorb W 80-100 was used.

8-Chloro-4-cyclooctenyltellurium trichloride(IV). TeCl_4 (7.5 g, 27.8 mmol) was added with stirring to an ice-cold solution of *cis*, *cis*-1,5-cyclooctadiene (3.0 g, 27.7 mmol) in 50 ml of dry ethanol-free chloroform. After 12 h 6.7 g (64% yield m.p. 99–100°C) could be filtered off. IR $\nu_{\text{max}}^{\text{KBr}}$ (cm^{-1}): 1484m, 1435m, 1429m, 1353w, 1339w, 1245w, 1131m, 1082w, 1059m, 976w, 935m, 878m, 869w, 830w, 793s, 746s, 739s, 645w. Mass spectrum m/e (rel. intensity): 343 ($M - \text{Cl}$)⁺(2), 341(2), 310(2), 308(6), 306(5), 304(4), 272(8), 270(8), 260(12), 258(20), 256(20), 254(15), 252(8), 202(9), 200(21), 198(16), 196(7), 167(9), 165(29), 163(26), 161(14), 144(11), 143(9), 142(8), 130(11), 128(11), 118(9), 116(24), 109(21), 108(41), 107(100), 106(25), 105(31), 104(7), 103(13), 102(6), 101(11). ^{13}C NMR (proton noise decoupled, CDCl_3 , Me_4Si) δ 23.96, 25.43, 28.54, 38.39, 66.93, 82.82, 128.28, 129.73 ppm.

8-Ethoxy-4-cyclooctenyltellurium trichloride(VI). 8-Chloro-4-cyclooctenyltellurium trichloride (3.1 g, 8.2 mmol) was refluxed in 40 ml ethanol, for 1½ h. Cooling of the filtered solution (–15°C) caused separation of colourless prisms melting at 138–140°C. Yield 2.4 g (76%). IR $\nu_{\text{max}}^{\text{KBr}}$ (cm^{-1}): 3005w, 2940m, 1461w, 1441m, 1396w, 1368w, 1225w, 1200w, 1119w, 1060w, 1038s, 1029s, 975s, 902m, 848m, 800w, 730s, 670m. Mass spectrum m/e (rel. intensity): 353 ($M - \text{Cl}$)⁺ (12), 351(15), 318(25), 316(18), 314(12), 283(22), 282(42), 281(20), 280(40), 279(12), 278(28), 277(12), 151(15), 123(13), 109(12), 107(90), 106(37), 105(100). Analysis. Found: C, 30.95; H, 4.38; Cl, 27.20; Te, 32.53. $\text{C}_{10}\text{H}_{17}\text{Cl}_3\text{OTe}$ calcd.: C, 30.99; H, 4.42; Cl, 27.46; Te, 32.95%.

8-(2-Hydroxyethoxy)-4-cyclooctenyltellurium trichloride (VIII). 8-Chloro-4-cyclooctenyltellurium trichloride (0.20 g, 0.53 mmol) was heated with 2 ml of ethylene glycol for 5 min over a water bath. Cooling of the clear solution precipitated 0.19 g (90%) white crystals, which were recrystallized from acetonitrile, m.p. 108–110°C. IR $\nu_{\text{max}}^{\text{KBr}}$ (cm^{-1}): 3600–3100 s, 3010w, 2940m, 1525w, 1500m, 1475w, 1210w, 1160s, 1085m, 1060m, 1010w, 985m, 885m, 840m, 805w, 74745m. The ^1H NMR spectrum showed a multiplet for the olefinic protons at 5.80 ppm and multiplets for the protons CHO and CHTe at 4.95 and 4.22 ppm, respectively. The two non-cyclic methylene groups appeared poorly resolved at 3.90 ppm. The 9 remaining protons were poorly resolved in the range from 2.70 to 2.00 ppm.

Oxidation of *cis*-2-butene. *cis*-2-Butene (2.0 g, 35.7 mmol), TeO_2 (3.0 g, 18.8 mmol) and LiBr (1.5 g, 17.2 mmol) were heated with 35 ml HOAc in a sealed tube at 90°C for 20 h. The mixture containing precipitated tellurium was poured into 100 ml H_2O , neutralized with NaHCO_3 and extracted with 2 × 50 ml ether. The ethereal solution, after drying over CaCl_2 , and evaporation, yielded 0.75 g 2,3-butanediol monoacetate (16.0%) and 1.20 g 2,3-butanediol diacetate

(19.3%). Yields were determined with a preparative SiO_2 -TLC plate using ethylacetate/hexane 2/1 as eluent and the products were compared to original samples. The *meso/d*, *l*-ratio was determined gas-chromatographically and found to be: for the diol diacetates *meso/d*, *l* 89/11, for the diol monoacetates (after acetylation in refluxing acetic anhydride) *meso/d*, *l* 91/9.

Oxidation of *trans*-2-butene. *trans*-2-Butene (2.0 g, 35.7 mmol), TeO_2 (3.0 g, 18.8 mmol) and LiBr (1.5 g, 17.2 mmol) were heated with 35 ml HOAc in a sealed tube at 90°C for 20 h. The mixture, which contained precipitated tellurium, was poured into 100 ml H_2O , neutralized with NaHCO_3 , and extracted with 2 x 50 ml ether. The ethereal solution was dried over CaCl_2 and evaporated to give 1.00 g 2,3-butanediol monoacetate (21.1%) and 0.57 g 2,3-butanediol diacetate (9.2%). Yields were determined with a preparative SiO_2 -TLC-plate using ethylacetate/hexane(2/1) as eluent, and the products were compared with authentic samples. The *meso/d*, *l*-ratio was determined gas-chromatographically and found to be: for the diol diacetates *meso/d*, *l* 35/65, for the diol monoacetates (after acetylation in refluxing acetic anhydride) *meso/d*, *l* 33/67.

Oxidation of 1-decene and *Z*-1-deuterio-1-decene. 1-Decene (1.0 g, 7.1 mmol), TeO_2 (2.0 g, 12.5 mmol) and LiBr (1.0 g, 11.5 mmol) were refluxed in 40 ml HOAc for 12 h. The mixture, which contained precipitated tellurium, was poured into 100 ml H_2O , neutralized with NaHCO_3 , and extracted with 2 x 50 ml ether. The ethereal solution was dried over CaCl_2 and evaporated to give 1.6 g pure (by GLC and NMR analysis) 1,2-decanediol diacetate (87%).

Z-1-Deuterio-1-decene was oxidized in the same way to yield the corresponding diol diacetate, with a ^1H NMR spectrum containing two doublets for the H(1)-proton at δ 3.95 ppm and δ 4.60 ppm, the integration ratio being 1/1.

Reduction of 4 with $\text{Na}_2\text{S}_2\text{O}_5$. An ether suspension of 0.3 g 8-chloro-4-cyclooctenyltellurium trichloride was shaken with an aqueous solution of 1.0 g $\text{Na}_2\text{S}_2\text{O}_5$ for a few minutes, during which elemental tellurium separated. Drying of the ether solution with CaCl_2 and evaporation yielded pure *cis*, *cis*-1,5-cyclooctadiene, as revealed by GLC and NMR analysis.

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