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DOMINANT *cis*-DIACETOXYLATION OF ALKENES WITH TELLURIUM(IV) OXIDE AND LITHIUM BROMIDE IN ACETIC ACID

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Summary

Oxidation of alkenes with tellurium(IV) oxide and lithium bromide in acetic acid affords the corresponding α,β-diacetoxyalkanes in good yields after acetylation of the primary products with acetic anhydride/pyridine. From cyclic alkenes such as cyclopentene, cyclohexene, cycloheptene, and 1,4-cyclohexadiene, the *cis*-diacetate is obtained as almost the sole product. In the cases of linear *cis*-alkenes such as *cis*-2-octene and *cis*-4-octene *cis*-stereochemistry is also preferred (*cis*/*trans* = 87 ~ 89/13 ~ 11), while the proportion of the *cis*-product is decreased in the cases of the corresponding *trans*-alkenes (*cis*/*trans* = 56 ~ 58/44 ~ 42). Transformation of a C–Te bond to a C–OAc bond under these reaction conditions is shown unambiguously by using β-chloroalkyltellurium(IV) trichlorides ($TeCl_4$ adducts of alkenes) and β-oxyalkyl phenyl tellurides (oxytellurenylation products of alkenes), *cis*-diacetates being solely formed from the *trans*-tellurium compounds in a cyclohexyl system. One of the possible reaction pathways for the oxidation is proposed which involves the acetoxy-, hydroxy-, and/or halogeno-tellurinylation of a double bond followed by an S_N2 type acetolysis of the produced C–Te bond.

Introduction

In connection with Oxirane's ethylene glycol process which involves a catalytic system of tellurium oxide/bromine compounds for direct oxidation of ethylene with oxygen in acetic acid, it has been reported that a combination of tellurium(IV) oxide and alkali metal halide or iodine can be used for oxidation of alkenes to vicinal diacetates [1,2] and also for selective 1,4-diacetoxylation of conjugated dienes in acetic acid [3]. In the alkene oxidation Bergman and Engman declared that the stereochemistry of the products depends on the alkene structure; thus, diacetates from *cis*- and *trans*-2-butenes were *cis*-rich, while no stereospecificity was found in the products from 1-deuterio-1-decene [1]. They postulated β-halogenoalkyltellurium(IV) compounds as intermediates. We were interested in the stereochemistry

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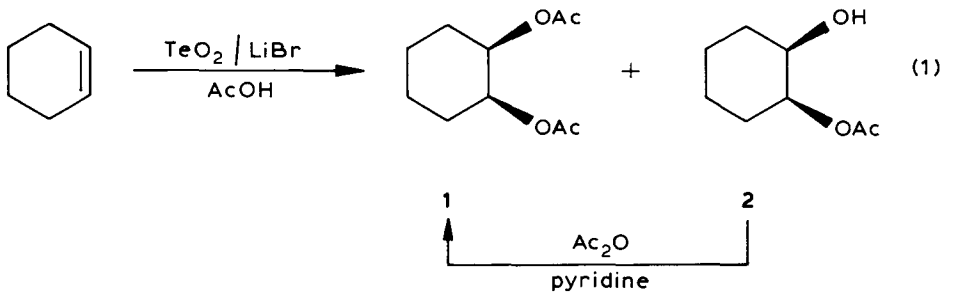


of the products, diacetates, from a synthetic viewpoint [4] as well as the reaction mechanism of this oxidation, and carried out further work on this subject [2]. As a result, it became clear that *cis*-diacetoxylation predominates in many alkenes, especially cyclic ones, that a nucleophilic conversion of a C–Te bond to a C–OAc bond occurs in several β-acetoxy-, β-hydroxy-, and β-chloro-alkyltellurium compounds under these acetoxylation conditions; *cis*-diacetates being solely formed from the *trans*-tellurium compounds in a cyclohexyl system. New evidence presented here supports the assumption of the intervention of organotellurium compounds as intermediates in this oxidation [1,5]. We describe here the results and discuss the reaction pathway.

Results and discussion

A mixture of cyclohexene (2 equiv.), tellurium(IV) oxide (1 equiv.), lithium bromide (1 equiv.), and acetic acid was refluxed for 20 h. The reaction mixture was orange-colored and heterogeneous, and elemental tellurium was deposited as a black precipitate as the reaction proceeded. After normal work-up, GLC analysis of the organic products revealed that they consisted of a major compound and a variable amount of a minor compound (less than 25% of the major by GLC), IR and ^1H NMR spectra showed them to have strong absorptions due to the hydroxy and acetoxy groups. Small amounts of *trans*-1-acetoxy-2-bromocyclohexane and 1,4-diacetoxy-2-cyclohexenes were also detected by GLC. When the products were treated with acetic anhydride/pyridine at 110–120°C for 1 h, only the minor compound described above was converted to the major compound which was revealed to be *cis*-1,2-diacetoxycyclohexane (**1**). The corresponding *trans*-diacetate could not be detected by GLC, but ^{13}C NMR measurement showed the presence of traces ($< 0.5\%$). With a short reaction time (2 h) the result was reversed, i.e., the minor product (mentioned above) became the major and was identified as *cis*-1-acetoxy-2-hydroxycyclohexane (**2**) (eq. 1). These results show that **2** is initially formed and then it is acetylated to **1** by prolonging the reaction time. The hydroxy group must have come from water which was probably present in traces in the acetic acid which we used as purchased, and in lithium bromide which is very hygroscopic. Actually, the use of aqueous acetic acid (10% H_2O) as the solvent resulted in a preponderance of **2** even after 20 h, although the total yield of **1** and **2** was lower. The formation of both monoacetate and diacetate as the products, their ratio to one another being dependent on the reaction time were also observed in the oxidation of 1-decene, the products being **9** and **10** together with a small amount of **11**. In order to simplify

TABLE 1

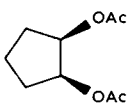
DIACETOXYLATION OF ALKENES WITH TeO_2/LiBr IN AcOH [a]

Alkene	Reaction temp. (°C)	Reaction time (h)	Product and yield (mmol) [b]			
Cyclopentene	120	20	**3**	13.7		
Cyclohexene	120	2	**1**	0.64 [c]	**2**	5.22 [c]
Cyclohexene	120	20	**1**	8.25 [c]	**2**	2.15 [c]
Cyclohexene [d]	120	20	**1**	1.68 [c]	**2**	2.88 [c]
Cyclohexene	80	20	**1**	1.66 [c]		
Cycloheptene	120	20	**4**	9.0(11.8) [c]		
Styrene	120	20	**5**	8.44		
Styrene	80	20	**5**	trace		
1-Octene	120	20	**6**	16.0		
cis-2-Octene	120	20	**7**	16.7 (*erythro/threo* 87/13)		
trans-2-Octene	120	20	**7**	18.3 (*erythro/threo* 42/58)		
cis-4-Octene [e]	120	20	**8**	8.7 (*meso/dl* 89/11)		
trans-4-Octene [e]	120	20	**8**	6.5 (*meso/dl* 44/56)		
1-Decene	120	5	**9**	5 6 [c]	**10** [f]	7.0 [c]
1-Decene	120	20	**9**	10.5 [c]	**10** [f]	2.3 [c]
Allyl acetae	120	20	**12**	11.7		
Allylbenzene	120	20	**13**	12.4		
1,4-Cyclohexadiene	120	20	**14**	10.3		

[a] Alkene (20 mmol), TeO_2 (10 mmol), LiBr (10 mmol), and AcOH (30 ml) were used, unless otherwise stated. [b] Isolated yield by distillation after acetylation, unless otherwise stated. [c] Determined by GLC before acetylation. [d] Solvent, AcOH (27 ml)/H_2O(3 ml). [e] The reaction was carried out on a half scale. [f] Contains 15–20% of **11** by ^1H NMR analysis.

product analysis, the primary products were generally acetylated as described above, then analyzed. The results of cyclopentene, cyclohexene, cycloheptene, styrene, 1-octene, *trans*- and *cis*-2-octenes, *trans*- and *cis*-4-octenes, 1-decene, allyl acetate, allylbenzene, and 1,4-cyclohexadiene are summarized in Table 1, the products being **1**–**14**. Oxidation was very slow at 80°C and it did not proceed at all when TeO_2 or LiBr were absent, even at reflux temperature. The addition of more than 1 equiv. of LiBr to TeO_2 had no appreciable effect on the product yield, stereoselectivity, or the ratio of monoacetate to diacetate [6]. Tellurium(VI) oxide (TeO_3) and telluric acid (H_6TeO_6) could also be used in place of TeO_2 for preparing *cis*-diacetate. For example, 9.6 and 6.4 mmol of **1** were formed from cyclohexene by using TeO_3 and H_6TeO_6, respectively, under such conditions where 10.4 mmol of **1** was obtained by using TeO_2 (GLC analysis). As can be seen from the Table, diacetoxylation prefers a *cis*-stereochemistry, especially in the cases of cyclic alkenes (~ 100%) and linear *cis*-alkenes (~ 90%), while with linear *trans*-alkenes the preference for the *cis*-product is lowered. All the corresponding *trans*-diacetates were prepared by a reported method [4] and used as authentic samples for GLC and spectral analyses.

As to the reaction pathway of this oxidation, the following three possibilities may be considered [1,7]; (i) a route involving a cyclic tellurium ester (**A**) as an intermediate analogous to that in the MnO_4^- and the OsO_4 oxidation of alkenes, (ii) a route involving some organotellurium compounds (**B**) derived from acetoxy- hydroxy-, and/or halogenotellurinylation of alkenes, (iii) a route via *vic*-bromoace-



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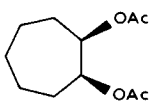

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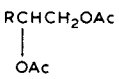
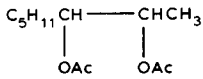


(5) R = Ph
(6) R = C_6H_{13}
(9) R = C_8H_{17}
(12) R = CH_2OAc
(13) R = $PhCH_2$



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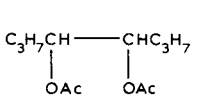

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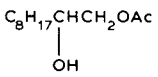

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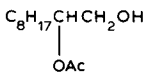

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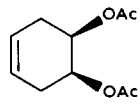

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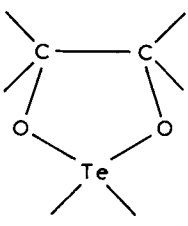
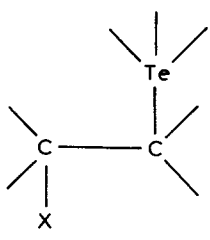


(A)



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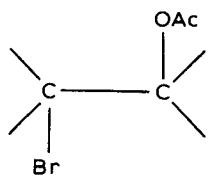
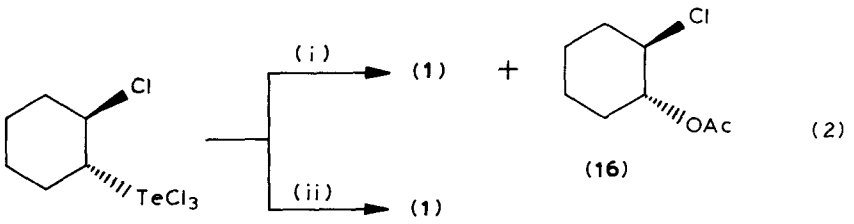


(C)

tates (**C**) formed by oxidative bromination of alkenes, bromine being produced by the oxidation of the bromide anion by Te(IV).

Bergman and Engman [1] have eliminated the pathway via **A** because of the stereochemistry of the products and the postulation that β-halogenoalkyltellurium(IV) compounds (**B**; X = halogen) are intermediates. They achieved a facile substitution of a chlorine atom on an alkyl carbon of the $TeCl_4$-1,5-cyclooctadiene adduct by an alkoxy group with complete retention of configuration, while we obtained direct evidence of the displacement of a tellurium moiety by an alkoxy or acetoxy group by the treatment of *trans*-2-chlorocyclohexyltellurium(IV) trichloride **15** with acetic acid [2a]. Patent work has also shown such an example using bis(2-bromoethyl)tellurium(IV) diacetate [5,8]. In order to obtain more evidence for the displacement of a C–Te bond and C–X bond (X = halogen) to a C–OR (R = H, Ac) bond and its stereochemistry, we carried out some experiments on the behaviour of $TeCl_4$-alkene adducts and oxytellurenylation products of alkenes towards acetic acid under similar conditions to those employed for the oxidation.

First, treatment of the $TeCl_4$-cyclohexene adduct (**15**) with acetic acid at reflux temperature for 20 h afforded **1** as the major product (20%), together with



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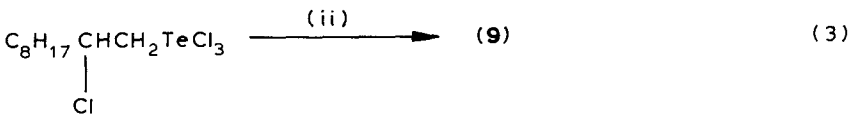
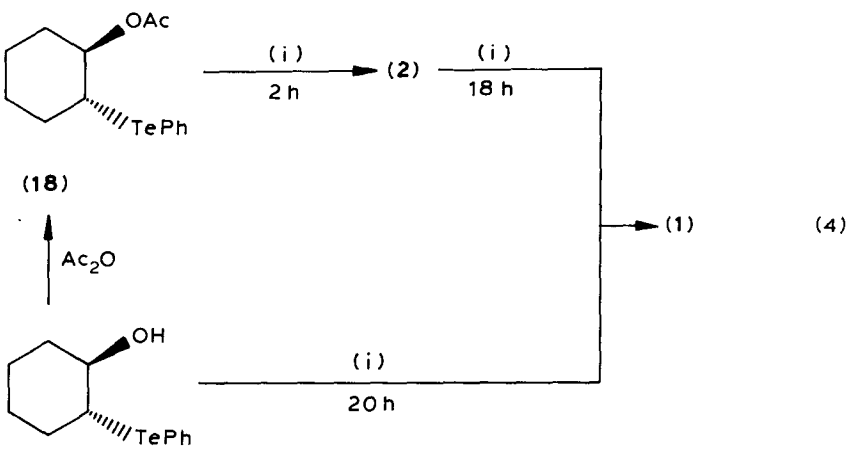


(3)

(17)

(i) AcOH ; reflux , 20 h

(ii) TeO_2-LiBr, AcOH ; reflux , 20 h



(4)

(i) TeO -LiBr, AcOH ; reflux

trans-1-acetoxy-2-chlorocyclohexane (**16**) (12%) and small amounts of two unidentified compounds (probably isomeric diacetoxycyclohexenes (by GLC) (eq. 2), while in the presence of TeO_2 and LiBr **1** was almost the sole product. The transformation was very slow, after 2 h only small amounts of the above products were produced, with or without TeO_2 and LiBr. Formation of *cis*-diacetate, **1** from the *trans*-compound **15** can be explained by the retentive acetolysis of a C–Cl bond [1] followed by a direct S_N2 attack by an acetoxy group on a C–Te bond. In all cases *trans*-1,2-diacetoxycyclohexane was not formed. The transformation of both C–Cl

TABLE 2

TRANSFORMATION OF A C–Te BOND OF ORGANOTELLURIUM COMPOUNDS INTO A C–OR (R = H, Ac) BOND [a]

Organotellurium compound (mmol)		TeO_2 (mmol)	LiBr (mmol)	AcOH (ml)	Reaction time (h)	Product and yield [b] (mmol)			
15	2	0	0	30	2	**16**	0.02	**2**	0.07 [c]
15	2	0	0	30	20	**16**	0.20	**1**	0.39 [c]
15	2	5	5	30	2	**16**	0.03	**2**	0.05 [c]
15	2	5	5	30	20	**1**	0.30 [c]		
17	1	0	0	10	20	**9**	0.11 [d]		
17	2	5	5	10	20	**9**	0.57 [d]		
18	2	5	5	20	2	**2**	0.82 [e]		
18	2	10	10	30	20	**1**	1.51 [e]		
19	2	10	10	30	20	**1**	0.46 [e]		

[a] Under reflux in AcOH (bath temp. 120–130°C). [b] Determined by GLC. [c] Small amounts of two unidentified compounds (probably isomeric diacetoxycyclohexenes) were detected by GLC. [d] Small amounts of four to six unidentified compounds were detected by GLC. [e] Isolated yield by column chromatography.

and C–Te bonds to C–OAc bonds was also observed in the case of the $TeCl_4$-1-decene adduct (**17**) (eq. 3).

Second, oxytellurenylation products of cyclohexene, *trans*-2-acetoxycyclohexyl phenyl telluride (**18**) and *trans*-2-hydroxycyclohexyl phenyl telluride (**19**), were converted to **1** and/or **2** by treatment with acetic acid under reflux in the presence of TeO_2 and LiBr (eq. 4). The conversion of **18** was much faster than that of **19**. Thus, **18** was transformed to **2** in 40% yield after 2 h, while only small amounts of **1** and **2** were obtained from **19** under the same conditions. By prolonging the reaction time to 20 h **1** was the only product, obtained either from **18** or **19** in 75% or 23% yield respectively, **1** was probably formed by the acetylation of **2** produced during the initial stages of the reaction. Formation of only the *cis*-product (**2**) suggests a direct S_N2 attack of a hydroxy group on the alkyl C–Te bond of **18**. No *trans*-diacetate was produced in these cases, either. Typical results of eqs. 2–4 are shown in Table 2.

Thus, we can present several examples which support a route via **B** for this alkene oxidation; namely, bromo-, hydroxy-, or acetoxytellurinylation of alkenes followed by acetolysis or hydrolysis of the C–Br or C–Te bonds. On the other hand, a path via **C**, i.e. via oxidative bromination of alkenes, does not seem to be involved in the main course of this oxidation from the following observations:

(1) The reaction of cyclohexene (4 equiv.) with bromine (1 equiv.) and TeO_2 (1 equiv.) in acetic acid under reflux for 2 h afforded *trans*-1,2-dibromocyclohexane (0.78 equiv.) and *trans*-1-acetoxy-2-bromocyclohexane (0.29 equiv.) as the main products, together with cyclohexyl bromide, but without the formation of **1** and **2**. Similarly, treatment of a mixture of *trans*-1,2-dibromocyclohexane and *trans*-1-acetoxy-2-bromocyclohexane (2 equiv., 82 : 18) prepared separately, with TeO_2 (1 equiv.) in acetic acid under reflux for 3 h resulted in the recovery of the initial reaction mixture almost intact, **1** and **2** were not formed.

(2) The reaction of *trans*-2-octene (2.4 equiv.) with bromine (1 equiv.) and TeO_2 (1 equiv.) in acetic acid under reflux for 20 h gave (**7**) (0.88 equiv., *erythro / threo* =

49/51) together with 2,3-dibromooctane (0.35 equiv.) and regioisomeric 2,3-acetoxybromooctanes (0.42 equiv.), the isomer ratio of **7** was different from that obtained in the TeO_2/LiBr system (42/58).

(3) Treatment of a mixture of 2,3-dibromooctane and isomeric 2,3-acetoxybromooctanes (1.8 equiv., 88 : 12), prepared separately from *cis*-2-octene, with TeO_2 (1 equiv.) in acetic acid under reflux for 20 h afforded **7** (0.1 equiv., *erythro*/*threo* = 55/45) in a low yield, a large portion of the starting materials were changed into tarry materials. The isomer ratio of **7** observed here was quite different from that obtained from the direct oxidation of *cis*-2-octene with TeO_2/LiBr (87/13).

Another possibility may be that tellurium tetrabromide is formed in situ from TeO_2 and LiBr and works as a reactive species for the oxidation. Such a route, however, was ruled out by the following result. Treatment of cyclohexene with commercial $TeBr_4$ in acetic acid under reflux for 2 h afforded cyclohexyl bromide, *trans*-1,2-dibromocyclohexane, and *trans*-1,2-diacetoxycyclohexane in fair yields, none of them being obtained in appreciable amounts after oxidation with TeO_2/LiBr. It has already been noted that neither $TeBr_4$ nor $TeBr_3^+$ was involved in the main reaction of the oxidation of conjugated dienes by a similar system [3].

Experimental

^1H NMR spectra were recorded with JEOL JNM FX-100 (100 MHz) and JEOL JNM GX-400 (400 MHz) instruments, in $CDCl_3$ solutions with Me_4Si as internal standard. ^{13}C NMR spectra were obtained at 25.1 MHz by use of a JEOLCO ^{13}C Fourier transform NMR system (JNM FX-100), in $CDCl_3$ solutions after 250–1000 pulses with intervals of 2.7–2.8 s. IR spectra were recorded with a JASCO IR-810(400–4000 cm^{-1}) spectrometer (neat). GLC analyses were carried out using a Yanagimoto G 2800 apparatus on EGSS-X(15%)-Chromosorb-W(1 and 3 m), Silicone DC QF-1(5%)-Chromosorb-W(1 m), and PEG 6000(25%)-Chromosorb-W (1 and 3 m) columns (N_2 as carrier gas). Mass spectra were recorded on a JEOL JMN-01SG spectrometer. Melting points were determined with a Yanagimoto MP micro melting point determination apparatus and were uncorrected.

Commercially available acetic acid, alkenes, and all other organic and inorganic compounds were used without further purification. Compounds **15** (m.p. 115–117 °C (dec)) and **17** (oil) were prepared by the reaction of cyclohexene and 1-decene with $TeCl_4$ in CCl_4 or $CHCl_3$ respectively by a reported method [9]. Compounds **1**, **5**, **6**, **9**, **16**, and *trans*-1,2-diacetoxycyclohexane were prepared by the acetylation of the corresponding commercial diols and alcohols, thus providing authentic samples for GLC and NMR analyses. Similarly, *trans*-isomers of **3**, **4**, and **14**, *erythro*-(**7**), and *meso*- and *dl*-(**8**) were prepared separately by a reported method [4] by oxidation of the corresponding alkenes with $FeSO_4 \cdot 7H_2O$ and $(NH_4)_2S_2O_8$ in acetic acid at 80 °C for 4 h. The characterization of diacetoxycyclohexenes has already been reported [3b]. Other oxidation products were isolated by distillation and/or column chromatography and characterized spectroscopically. Compounds **7**, **14**, **18**, and **19** are new.

*Preparation of 2-hydroxycyclohexyl phenyl telluride (**19**) and 2-acetoxycyclohexyl phenyl telluride (**18**)*

Diphenyl ditelluride (6.20 g, 15.1 mmol) and sodium borohydride (1.75 g, 46.3

mmol) were placed in a two-necked flask, under N_2, and ethanol (35 ml) was added by injection through a rubber septum. Cyclohexene oxide (3.04 g, 31.0 mmol) in ethanol (10 ml) was then added in a similar way and the resulting mixture was stirred under reflux for 4 h. The mixture was cooled, treated with brine, and then extracted with $CHCl_3$ (3×50 ml). After being dried over $MgSO_4$, the solvent was evaporated to leave a yellow oil which was subjected to column chromatography on SiO_2 to give diphenyl ditelluride (0.17 g, 0.4 mmol) (elution with hexane) and **19** (yellow syrup, 8.42 g, 27.7 mmol, 92% yield) (elution with hexane : ethyl acetate (10 : 1)). Compound **19**; δ(H) (100 MHz) 1.0–1.85 (6H, m), 1.95–2.40 (2H, m), 2.74 (1H, br s, exchangeable in D_2O, OH), 3.10 (1H, td, *J* 10.3 and 3.9 Hz), 3.42 (1H, td, *J* 10.3 and 3.9 Hz), 7.05–7.36 (3H, m), 7.68–7.88 (2H, m) ppm; ν_{max}(neat) 3400 br s, 3060, 3050, 2930s, 2850s, 1570, 1470s, 1450s, 1435s, 1350, 1320, 1300, 1270, 1250, 1160, 1100, 1060s, 1020s, 1000, 950s, 860, 835, 735s, 695s cm^{-1}. Anal. Found: C, 47.15; H, 5.15. $C_{12}H_{16}OTe$ calcd.: C, 47.43; H, 5.31%. ^1H NMR spectrum was identical with that of the compound obtained by N_2H_4 reduction of *trans*-(2-hydroxycyclohexyl)phenyltellurium dibromide [10].

The telluride **19** (5.17 g, 17.0 mmol) was dissolved in pyridine (30 ml) containing acetic anhydride (3.02 g, 29.6 mmol) and the mixture stirred at 50–60°C for 2 d. The mixture was cooled and aqueous Na_2CO_3 was added. The aqueous layer was then extracted with $CHCl_3$ (3×50 ml). The extract was washed with aqueous HCl (1*M*) and brine and dried ($MgSO_4$). Evaporation of the solvent left a dark-red oil which was subjected to column chromatography on SiO_2 to give diphenyl ditelluride (0.27 g, 0.7 mmol) (elution with hexane), **18** (red syrup, 3.56 g, 61% yield) (hexane: ethyl acetate (10 : 1)). Compound **18**; δ(H) (100 MHz) 1.1–1.8(6H, m), 1.98(3H, s), 2.0–2.35(2H, m), 3.34(1H, td, *J* 9.7 and 3.9 Hz), 4.88(1H, td, *J* 9.7 and 3.9 Hz), 7.08–7.34 (3H, m), 7.68–7.88(2H, m) ppm; ν_{max}(neat) 3060, 3050, 2930s, 2850s, 1740vs, 1570, 1475, 1450s, 1435s, 1375s, 1240vs, 1200, 1170, 1035s, 1020, 1000, 960, 940, 905, 850, 800, 735s, 695s cm^{-1}. Anal. Found: C, 48.67; H, 5.31. $C_{14}H_{18}O_2Te$ calcd.: C, 48.61; H, 5.25%.

*Authentic samples of 1-acetoxy-2-hydroxydecane (**10**) and 2-acetoxy-1-hydroxydecane (**11**)*

1,2-Epoxydecane (1 g), prepared by epoxidation of 1-decene with *m*-chloroperbenzoic acid in ethyl acetate at 0–20°C for 24 h, was heated in acetic acid (5 ml) at 60–70°C for 24 h as reported for the preparation of 1,2-octanediol monoacetates [11]. Brine was added to the solution and the aqueous layer was extracted with $CHCl_3$(3×30 ml). The extract was washed with aqueous $NaHCO_3$ and brine, and dried($CaSO_4$). Evaporation of the solvent left a pale yellow oil, which upon Kugelrohr distillation, afforded a mixture of (**10**) and (**11**) as a colorless liquid (0.95 g, 69% yield, b.p. 200°C/2 Torr) The mixture gave a homogeneous peak with GLC, while analysis of the ^1H NMR spectrum, which closely resembles that of the 1,2-octanediol monoacetates [11], revealed that the isomer ratio of **10** : **11** was 65 : 35; **10** and **11**, δ(H) (100 MHz) 0.88(t), 1.10–1.70(m), 2.10(s), 2.25(br s, exchangeable in D_2O, OH), 3.60–4.28(m, $CHCH_2$ of **10** and CH_2 of **11**), 4.79–5.08(m, CH of (**11**)) ppm; ν_{max}(neat) 3450br s, 2930s, 2860s, 1740s, 1730sh, 1470, 1375, 1245s, 1130, 1100sh, 1045 cm^{-1}. Anal. Found: C, 66.38; H, 10.97. $C_{12}H_{24}O_3$ calcd.: C, 66.63; H, 11.18%.

Oxidation of cyclohexene with TeO_2 and LiBr in acetic acid

The following example is a typical experimental procedure for the oxidation of an alkene.

To a mixture of TeO_2 (1.60 g, 10 mmol), LiBr (0.87 g, 10 mmol), and acetic acid (30 ml) was added cyclohexene (1.64 g, 20 mmol) at room temperature. The resulting yellow-orange heterogeneous mixture was stirred, and heated under reflux for 20 h, during which, the mixture gradually became a blackened suspension. The mixture was cooled and the solids were filtered off. The filtrate was treated with brine and then extracted with $CHCl_3$(3×50 ml): The extract was washed successively with aqueous $NaHCO_3$ and brine, and then dried over $MgSO_4$. GLC analysis of the extract revealed the presence of **1** and **2** (79 : 21 by peak area ratio) together with small amounts of *trans*-1-acetoxy-2-bromocyclohexane and diacetoxycyclohexenes [3b]. Evaporation of the solvent left an oily residue, of which the IR spectrum showed strong absorptions at 3450, 1740, and 1240 cm^{-1}, due to the hydroxy and acetoxy groups. The residue was then treated with acetic anhydride (3 ml) in pyridine (7 ml) at 120°C for 1 h. GLC analysis of the pyridine solution using benzyl acetate as internal standard revealed the presence of **1** (2.08 g, 10.4 mmol), and none of **2**, other minor compounds remaining. For the isolation of **1** the pyridine solution was made slightly acidic using aqueous HCl and then extracted with $CHCl_3$(3×30 ml). The extract was treated as described above and Kugelrohr distillation afforded 1.50 g of almost pure **1**, b.p. 160–165°C/3 Torr; δ(H) (100 MHz) 1.2–1.9 (8H, m), 2.06(6H, s), 5.00(2H, d); δ(C) 21.1(q), 21.7(t), 27.6(t), 70.9(d), 170.3(s) ppm; ν_{max}(neat) 2940, 2870, 1740vs, 1450, 1370, 1255vs, 1235vs, 1125, 1055, 1020, 985, 955 cm^{-1}. For comparison, the *trans*-isomer of **1**, δ(H) (100 MHz) 1.2–1.9(8H, m), 2.04(6H, s), 4.80 (2H, br); δ(C) 21.1(q), 23.4(t), 30.1(t), 73.7(d), 170.4(s) ppm.

Isolation of cis-1-acetoxy-2-hydroxycyclohexane **2** *and trans-1-acetoxy-2-bromocyclohexane*

A mixture of cyclohexene (1.64 g, 20 mmol), TeO_2 (1.60 g, 10 mmol), LiBr (3.48 g, 40 mmol), and acetic acid (30 ml) was stirred at reflux temperature for 2 h, and then treated as above. Evaporation of the solvent from $CHCl_3$ extract left an oily residue, column chromatography on SiO_2 afforded four fractions: (i) an unidentified compound, 0.073 g (elution with hexane), (ii) *trans*-1-acetoxy-2-bromocyclohexane, 0.173 g (0.78 mmol) (hexane : ethyl acetate (10 : 1)), (iii) a mixture of **1** and diacetoxycyclohexenes, 0.345 g(hexane : ethyl acetate (5 : 1)), and (iv) **2**, 0.825 g (5.86 mmol) (ethyl acetate). **2**, δ(H) (100 MHz) 1.20–2.0(8H, m), 2.09(3H, s), 2.20(1H, br s, exchangeable in D_2O, OH), 3.75–3.95 (1H, m), 4.80–5.0(1H, m) ppm; ν_{max}(neat) 3450s, 2940s, 2860s, 1730vs, 1450, 1370s, 1240vs, 1075, 1040, 1020, 980 cm^{-1}. *trans*-1-Acetoxy-2-bromocyclohexane, δ(H) (100 MHz) 1.2–2.4(8H, m), 2.09(3H, s), 3.96 (1H, ddd, *J* 10.7, 9.3, and 4.4 Hz), 4.90(1H, td, *J* 9.8 and 4.4 Hz) ppm; *m/z* 180 and 178($M - CH_2CO$), 162 and 160($M - CH_3CO_2H$), 141(M − Br).

Spectroscopic data of other diacetates (**3**, **4**, **7**, **8**, **13**, **14**) are shown below together with those of several corresponding *trans*-diacetates. All samples showed very strong IR spectrum absorptions at about 1740 and 1240 cm^{-1}.

cis-1,2-Diacetoxycyclopentane (3), b.p. 220°C/24 Torr, δ(H) (100 MHz) 1.4–2.0(6H, m), 2.02 (6H, s), 5.12(2H, br m); δ(C) 19.2(t), 20.9(q), 28.3(t), 74.1(d), 170.4(s). The *trans*-isomer of **3**, prepared [4] in 39% isolated yield, b.p. 220°C/24 Torr, δ(H) (100 MHz) 1.5–1.9(4H, m), 2.0–2.3(2H, m), 2.02(6H, s), 4.96–5.14(2H, m); δ(C) 21.0(q), 21.5(t), 30.4(t), 78.9(d), 170.1(s) ppm.

*cis-1,2-Diacetoxycycloheptane (**4**)*, b.p. 220°C/22 Torr, δ(H) (400 MHz) 1.52–1.74(8H, m), 1.86–1.96(2H, m), 2.05(6H, s), 5.06–5.09(2H, m); δ(C) 21.1(q), 22.5(t), 26.6(t), 28.7(t), 74.4(d), 170.3(s) ppm. The *trans*-isomer of **4**, prepared [4] in 42% isolated yield, b.p. 220°C/22 Torr, δ(H) (400 MHz) 1.55–1.58(4H, m), 1.66–1.73(4H, m), 1.78–1.85(2H, m), 2.01(6H, s), 4.93–4.99(2H, m); δ(C) 21.1(q), 22.8(t), 28.3(t), 30.4(t), 76.9(d), 170.3 (s).

*erythro-2,3-Diacetoxyoctane (**7**)*, prepared in a pure form (60% isolated yield, b.p. 220°C/23 Torr) by oxidation of *trans*-2-octene by a reported method [4], δ(H) (100 MHz) 0.88(3H, t), 1.21 (3H, d), 1.10–1.70(8H, m), 2.02(3H, s), 2.06(3H, s), 4.84–5.12 (2H, m); δ(C) 13.9(q), 14.7(q), 20.9(q), 21.0(q), 22.5(t), 25.1 (t), 29.8(t), 31.6(t), 70.9(d), 74.5(d), 170.3(s), 170.5(s) ppm.

*threo-2,3-Diacetoxyoctane (**7**)*, isolated as a mixture with *erythro*-isomer (*threo : erythro* = 58 : 42), b.p. 190°C/6 Torr, δ(H) (100 MHz) 1.19(3H, d), 2.05(3H, s), 2.08(3H, s), other signals are identical with those of the *erythro*-isomer; δ(C) 13.9(q), 16.3(q), 20.9(q), 21.0(q), 22.5(t), 24.9(t), 30.4(t), 31.6(t), 70.6(d), 74.8(d), 170.3(s), 170.5(s) ppm. Anal. Found: C, 61.93; H, 9.58. $C_{12}H_{22}O_4$ calcd.: C, 62.58; H, 9.63%.

meso-4,5-Diacetoxyoctane (**8**), prepared in a pure form by a reported method [4] from *trans*-4-octene (83% isolated yield, b.p. 240°C/25 Torr), δ(H) (100 MHz) 0.8–1.04(6H, m), 1.14–1.74(8H, m), 2.04(6H, s), 4.90–5.10(2H, m); δ(C) 13.8(q), 18.8(t), 21.0(q), 31.3(t), 74.0(d), 170.6(s) ppm.

*dl-4,5-Diacetoxyoctane (**8**)*, isolated as a mixture with *meso*-isomer (*dl : meso* = 56 : 44), b.p. 240°C/25 Torr, δ(H)(100 MHz) 2.08(6H, s), other signals are almost identical with those of the *meso*-isomer; δ(C) 13.8(q), 18.5(t), 21.0(q), 32.9(t), 73.7(d), 170.6(s) ppm.

*1,2-Diacetoxy-3-phenylpropane (**13**)*, b.p. 250°C/4 Torr, δ(H) (100 MHz) 2.0(3H, s), 2.06 (3H, s), 2.90(2H, d, *J* 7 Hz), 3.99 (1H, dd, *J* 12 and 6.4 Hz), 4.24(1H, dd, *J* 12.2 and 3.4 Hz), 5.26(1H, qd, *J* 6.8 and 3.4 Hz), 7.04–7.26 (5H, m) ppm.

*cis-4,5-Diacetoxycyclohexene (**14**)*, b.p. 150–160°C/2 Torr, δ(H) (100 MHz) 2.04 (6H, s), 2.36 (4H, d, *J* 6 Hz), 5.16 (2H, tt, *J* 6 and 1 Hz), 5.60 (2H, t, *J* 1.5 Hz); δ(C) 21.1(q), 28.6(t), 69.0 (t), 123.6(d), 170.3(d) ppm. Anal. Found: C, 59.97; H, 7.14. $C_{10}H_{14}O_4$ calcd.: C, 60.59; H, 7.12%.

trans-Isomer of **14**, prepared [4] in 20% isolated yield, b.p. 220°C/5 Torr, δ(H) (100 MHz) 2.04(6H, s), 2.0–2.75(4H, m), 4.92–5.20(2H, m), 5.52–5.62(2H, m).

*Treatment of (**18**) with acetic acid*

A black heterogeneous mixture of **18** (0.69 g, 2 mmol), TeO_2 (1.60 g, 10 mmol), LiBr (0.88 g, 5 mmol), and acetic acid (30 ml) was stirred at reflux temperature for 20 h. The mixture was cooled and the grey solids (1.20 g) which separated were filtered off. The filtrate was treated in the same way as for cyclohexene oxidation, described above. GLC analysis of the $CHCl_3$ extract showed the presence of only one peak, and evaporation of $CHCl_3$ left an oily residue which was subjected to column chromatography on SiO_2 to give pure **1** (0.301 g, 1.51 mmol, 75.3% yield) (elution with hexane : diethyl ether(1 : 1)). ^1H and ^{13}C NMR spectra, and retention time (GLC) in two different columns, for **1** were identical with those of an authentic sample. Treatment of **15**, **17**, and **19** with acetic acid was carried out in a similar manner in the presence of, or without TeO_2 and/or LiBr.

Treatment of a mixture of bromination products of cis-2-octene with TeO_2 in acetic acid

A solution of bromine (3.2 g, 20 mmol) in acetic acid (15 ml) was added to a solution of *cis*-2-octene (2.24 g, 20 mmol, it contained 5% *trans*-isomer) in acetic acid (15 ml) at room temperature and the resulting pale yellow solution was stirred under reflux for 20 h. The mixture was treated with brine (200 ml) and extracted with $CHCl_3$ (3×40 ml), which had been washed with aq. $NaHCO_3$ and brine and dried ($MgSO_4$). Evaporation of the solvent left a pale-orange oil (5.03 g). GLC analysis using a Silicone DC QF-1(5%) column, revealed that it consisted of 2,3-dibromooctane (88%) and regioisomeric 2,3-acetoxybromooctanes (12%). The IR spectrum showed strong absorptions due to the acetoxy group.

This pale-orange oil (2.43 g, 9 mmol) and tellurium(IV) oxide (0.80 g, 5 mmol) were then stirred in acetic acid (30 ml) under reflux for 20 h. The black solids and a large amount of tarry products were filtered off, and the filtrate treated as above. GLC analysis of the $CHCl_3$ extract after treatment with acetic anhydride/pyridine revealed the presence of 2,3-dibromooctane (0.28 mmol), regioisomeric 2,3-acetoxybromooctanes (0.58 mmol), and 2,3-diacetoxyoctanes (**7**) (0.48 mmol, *erythro : threo* = 55 : 45).

Treatment of cyclohexene with $TeBr_4$

A mixture of $TeBr_4$ (Strem Chemicals) (4.47 g, 10 mmol), cyclohexene (1.64 g, 20 mmol), and acetic acid (30 ml) was stirred at reflux temperature for 2 h. The mixture quickly turned into a black suspension with evolution of HBr gas. It was cooled and the precipitated black solids (1.05 g) were filtered off, the filtrate was then treated as above ($CHCl_3$ extraction). GLC analysis of the $CHCl_3$ extract revealed the presence of cyclohexyl bromide, *trans*-1,2-dibromocyclohexane, *trans*-1,2-diacetoxycyclohexane, and one unidentified compound. Kugelrohr distillation (b.p. 200–240°C/20 Torr) afforded 1.37 g of distillate of this mixture with peak areas of 56 : 15 : 18 : 11 in that order, with 0.13 g of black-brown tarry compounds remaining. GLC analysis showed that neither **1** nor **2** were present.

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