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Diacetoxylation of nonconjugated dienes with TeO_2 and the isolation of intermediate organotellurium compounds

Yasuharu Yoshimori, Chan Sik Cho, Sakae Uemura *

Division of Energy and Hydrocarbon Chemistry, Graduate School of Engineering, Kyoto University, Sakyo-ku, Kyoto 606-01, Japan

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Abstract

Tellurium(IV) oxide (TeO_2) reacts with nonconjugated dienes in acetic acid at reflux temperature in the presence of lithium halide or iodine to give the corresponding *vic*-diacetates in moderate yields. When the reaction is carried out at 80°C and the reaction mixture is then reduced with aqueous sodium thiosulfate, *bis*(β-acetoxyalkyl)ditellurides are isolated as main products. Treatment of the ditellurides with refluxing acetic acid affords the corresponding *vic*-diacetates in good yields. The expected tellurium containing heterocyclic compounds, such as telluracyclopentanes and telluracyclohexanes, are not formed and/or isolated under the conditions employed. When 4-vinylcyclohexene and limonene are used as dienes in the diacetoxylation reaction, aromatic compounds due to the dehydrogenation of cyclohexene ring are also produced in moderate yields.

Keywords: Tellurium; Oxidation; Diolefin; Lithium halide; Iodine; Diacetoxylation

1. Introduction

Although tellurium(IV) oxide (TeO_2) is insoluble in many organic solvents and almost inactive for oxidation of organic compounds, it has been known that a combination of TeO_2 and lithium halide (LiX; X = Cl, Br) in acetic acid is quite useful for the oxidation of alkenes to vicinal diacetates [1,2], the selective 1,4-diacetoxylation of conjugated dienes [3], the cyclization of γ- and δ-hydroxyolefins [4], the synthesis of 3-halogenobenzo-[b]tellurophenes from phenylacetylenes [5], the oxidation of some nitrogen compounds [6] and the acetoxymethylation of certain aromatic compounds [7]. It is also known that TeO_2 itself oxidizes stilbene dibromides into benzils [8]. Bergman and Engman first suggested a mixed halide–acetate tellurium(IV) species **1** as a reactive species in these reactions [1,7]. In the alkene oxidation the species attacks alkenes electrophilically to give some β-hydroxy and/or β-acetoxyalkyltellurium compounds [2,4], a C–Te bond in which suffers an S_N2 attack of acetoxy group to give mainly *cis-vic*-diacetates [2] (Scheme 1). A similar pathway was also proposed and clarified in the $TeCl_4$/LiOAc/AcOH [9] system for alkene oxidation.

Since the tellurium containing heterocyclic compounds have been prepared from $TeCl_4$ or $TeBr_4$ and 1,5-diolefins or 1,6-diolefins [10,11], the formation of similar compounds via an intramolecular attack of a cationic tellurium species might be expected when the TeO_2/LiX oxidation system is applied to certain nonconjugated dienes. Although these compounds could not be formed and/or isolated, we succeeded in the isolation of several new (β-acetoxyalkyl)tellurium compounds having an alkene part in the same molecule. As one of our series of studies on alkene oxidation with the TeO_2/LiX system [2,3], we report here several new results of its application to certain nonconjugated dienes; *i.e.* diacetoxylation, an isolation of new organotellurium compounds, a facile conversion of a C–Te bond to a C–OAc bond and aromatization of the cyclohexene part.

2. Results and discussion

2.1. Diacetoxylation of dienes

A mixture of tellurium(IV) oxide (10 mmol), lithium bromide (10 mmol), and acetic acid (60 ml) was heated under reflux for 2 h. To the resulting orange colored heterogeneous mixture was added 4-vinylcyclohexene

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* Corresponding author.

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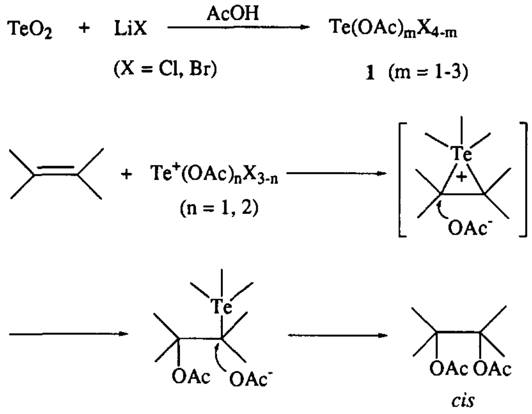
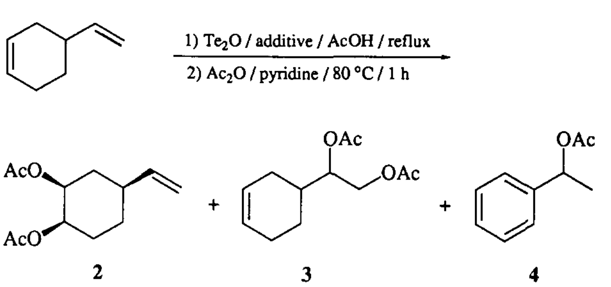


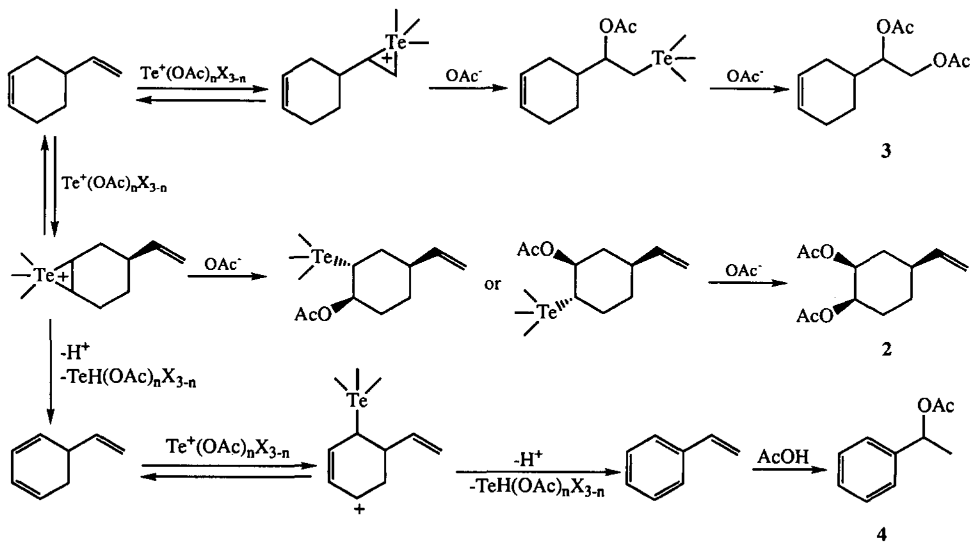
Scheme 1.

(10 mmol) and the mixture was heated under reflux with stirring for 5 h, during which period elemental tellurium was deposited as a black precipitate. After usual work-up procedure, GLC, ^1H NMR and IR analysis of the products in the CH_2Cl_2 extract showed the presence of diacetates and diol monoacetates. For convenience of the analysis, the products were treated with acetic anhydride (3 ml)/pyridine (7 ml) at 80°C for 1 h to acetylate any free hydroxy groups (Scheme 2). Results for the diacetoxylation reaction of 4-vinylcyclohexene under various conditions were shown in Table 1.

vic-Diacetates were produced as an isomeric mixture of *cis*-1,2-diacetoxy-*cis*-4-vinylcyclohexane (**2**) and 4-(1,2-diacetoxyethyl)cyclohexene (**3**). The stereochemistry of **2** was recognized by considering the vicinal coupling constant between the methine hydrogen on the two acetate carbons having an acetoxy group and the chemical shift of hydrogen on the carbon bearing a vinyl group. The corresponding *trans*-isomer (diacetate part) of **2**, prepared by oxidation of 4-vinylcyclohexene with $(NH_4)_2S_2O_8$ in acetic acid [12], was present only in a small amount (< 5% of **2** by GLC). The preferential formation of *cis*-diacetate is in accord with the reported results [2]. When lithium bromide or iodide was used as an additive, the isomer ratio between **2** and **3** was 22:78 (run 3) or 18:82 (run 6), while with iodine as an additive the ratio was 77:23 (run 8). Since the oxidation did not occur at all only with iodine (run 9), it is quite probable that TeO_2 and I_2 interact to give some reactive species different to those from TeO_2 and LiX. The different regioselectivity was also observed between oxidation using LiCl and that using LiBr and LiI; with the former the formation of **2** becoming predominant. This may be due to the difference of steric hinderence of a reactive species **1**: that is, a tellurium species from TeO_2 and LiBr or LiI is bulkier than that from LiCl, and so the attack occurs preferentially at the less hindered vinyl group than the double bond of six-membered ring. No *vic*-diacetates were obtained if lithium acetate was used in place of lithium halides (run 7). Longer reaction time more than 5 h (run 4) or the use of an excess of LiBr ($LiBr/TeO_2 = 5$) (run 5) decreased the yield of *vic*-diacetates, especially of **2**, by increasing the amount of some unidentified high-boiling compounds. The formation of these high-boiling compounds was also con-



Scheme 2.



Scheme 3.

firmed, but a lower amount, when the ratio LiBr/TeO_2 = 1 or the reaction time was less than 5 h. These results may show that the oxidation first occurred at one double bond to form the corresponding *vic*-diacetates **2** and **3** and this was followed by further oxidation of another double bond to form high-boiling compounds such as tetraacetates.

When lithium halide was used as an additive, the formation of 1-phenylethyl acetate (**4**) was always observed. Since aromatization of cyclohexene groups with $TeCl_4$ is known [11], it is quite probable that 4-vinylcyclohexene first aromatizes to styrene under our reaction conditions. In fact, over a reaction time of 2 h the formation of a small amount of styrene was observed (run 2). Acetic acid then readily reacts to form styrene giving **4**; this process was also confirmed in a separate experiment.

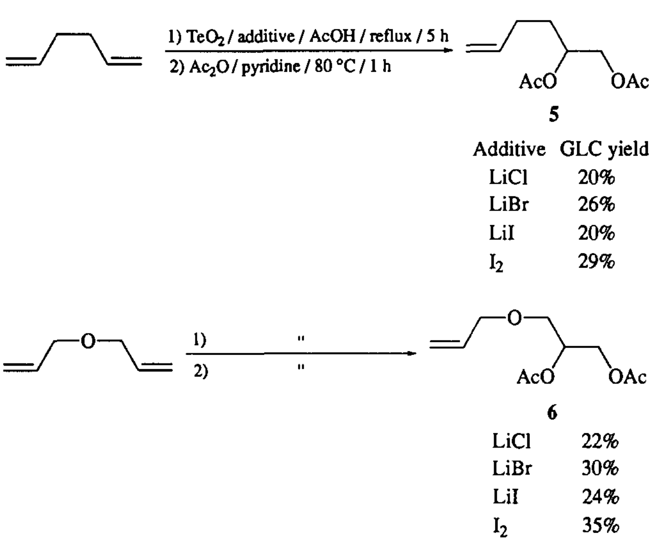
The speculative reaction pathway for the formation of the compounds **2–4** is as follows (Scheme 3). First, tellurium species attack carbon–carbon double bonds of 4-vinylcyclohexene electrophilically to form the corresponding organotellurium compounds, and then the *vic*-diacetates **2** and **3** are formed by a direct S_N2 attack of an acetoxy group on a C–Te bond. As to the formation of styrene and/or **4**, a recent report on aromatization of cyclohexene derivatives with $TeCl_4$ in $CHCl_3$ or CCl_4 is worth noting; the addition of a tellurium species to an alkene part followed by elimination of a proton and a tellurium moiety was proposed [11], as shown in Scheme 3. We do not have any new experimental evidence to add this speculation, but this seems to be the first example of aromatization using TeO_2.

Next, we carried out the oxidation of some other dienes such as 1,5-cyclooctadiene, 5-vinyl-2-norbornene and limonene. Neither *vic*-diacetates nor dehydrogenation products could be isolated and characterized from the oxidation of first two dienes. From limonene, however, 1-methyl-4-isopropenylbenzene was obtained in about 10% yield in a reaction as in the case of 4-vinylcyclohexene.

TABLE 1. Diacetoxylation of 4-vinylcyclohexene [a]

Run	Additive (mmol)	Reaction time (h)	Isolated yields (%) [b]	
			2+3 (2:3)	4
1	LiCl (10)	5	35 (57:43)	20
2 [c]	LiBr (10)	2	25 (18:82)	10
3	LiBr (10)	5	40 (22:78)	28
4 [d]	LiBr (10)	14	23 (11:89)	30
5 [d]	LiBr (50)	5	20 (9:91)	15
6	LiI (10)	5	38 (18:82)	18
7	LiOAc (10)	5	0	0
8	I_2 (10)	5	46 (77:23)	trace
9 [e]	I_2 (10)	5	0	0

[a] All reactions were carried out with 4-vinylcyclohexene (10 mmol), TeO_2 (10 mmol), and an additive (10 ~ 50 mmol) in AcOH (60 ml) at reflux unless otherwise stated. [b] Based on 4-vinylcyclohexene. [c] Styrene (~ 5%) was another identified compound. [d] Lots of high-boiling unidentified compounds were formed. [e] TeO_2 was not used.



Additive	GLC yield
LiCl	20%
LiBr	26%
LiI	20%
I_2	29%

LiCl	22%
LiBr	30%
LiI	24%
I_2	35%

Scheme 4.

Diacetoxylation of linear nonconjugated dienes such as 1,5-hexadiene and diallyl ether similarly gave the corresponding *vic*-diacetates **5** and **6** respectively (Scheme 4), authentic samples of which were prepared by a reported method [12] by the oxidation of the corresponding dienes with $(NH_4)_2S_2O_8$ in acetic acid. The product yields were always lower than that from 4-vinylcyclohexene and hardly affected by changing the kind of additives. In all cases high-boiling compounds were present and by prolonging the reaction time their yield was increased. Treatment of the isolated **5** and **6** under similar conditions resulted in the formation of such uncharacterized compounds. In any case of these diacetoxylation reactions, a new carbon–carbon bond formation via transannular reaction could not be observed.

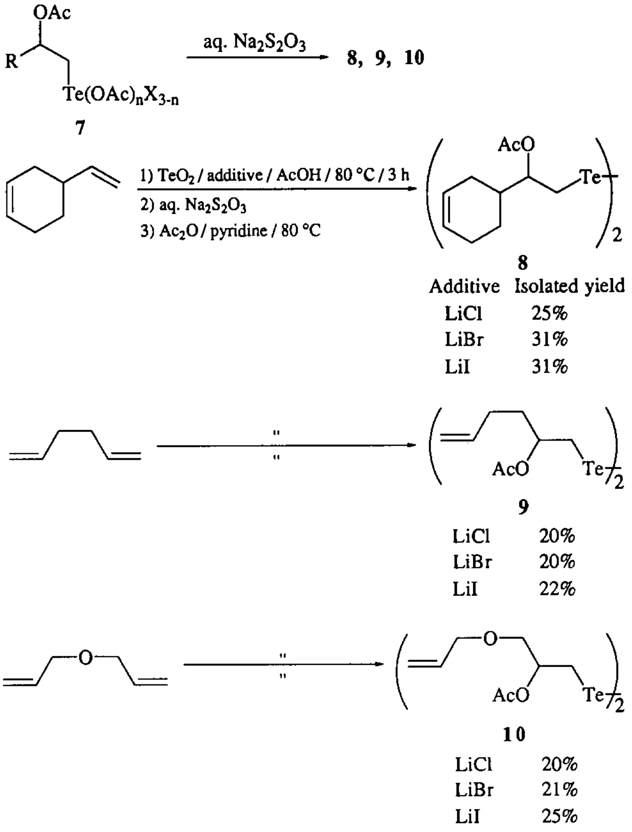
2.2. *Isolation of acetoxytelluration compounds from nonconjugated dienes*

A mixture of tellurium(IV) oxide (10 mmol), lithium bromide (10 mmol), and acetic acid (60 ml) was heated under stirring at 80°C for 2 h. To the resulting orange-colored heterogeneous mixture was added 4-vinylcyclohexene (10 mmol) and the mixture was heated at 80°C for another 3 h. After filtration of the insoluble gray to white solids, the filtrate was treated with aqueous sodium thiosulfate at room temperature for 10–30 min, during which period elemental tellurium was deposited as a black precipitate. The solution was then worked up in the same manner as for the diacetoxylation. GLC analysis of the CH_2Cl_2 extract did not show any formation of **2** and **3**. Evaporation of the solvent left an orange solid and a dark red oil. ^1H NMR, ^{13}C NMR and IR spectra of the orange solid showed it to be an inorganic compound. The formation of the same compound was also observed even without the addition of the alkene. This solid was unstable at room temperature in the air and decomposed with the deposition of elemental tellurium within a week. The dark red oil was found to be *bis*(β-acetoxyalkyl)ditelluride **8**. Similar treatment of nonconjugated dienes such as 1,5-hexadiene and diallyl ether also afforded similar ditellurides **9** and **10** in moderate yields (20%–31%) (Scheme 5).

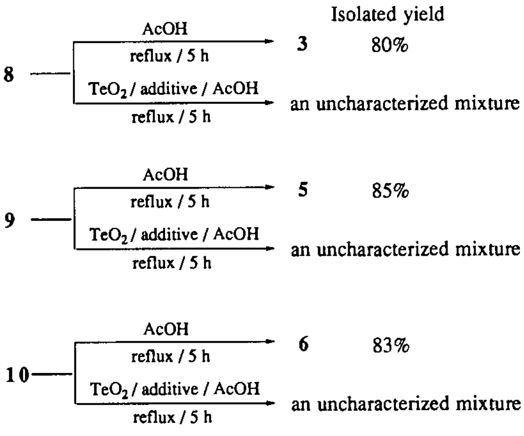
These compounds were formed only when lithium halide was used as an additive, and they were not obtained when I_2 was employed. The fact also shows that the reactive species and/or the reaction pathway using I_2 is different from the one using lithium halide. These ditellurides surely arose by the reduction of the intermediate acetoxytelluration compounds **7** as has already been clarified in the cyclization of γ- and δ-hydroxyolefins [4] or in the acetoxytelluration of alkenes with $TeCl_4$/LiOAc in acetic acid [9]. In any reactions at 80°C or under reflux the formation of the expected tellurium containing heterocyclic compounds such as telluracyclopentane or cyclohexane derivatives were not observed and/or confirmed.

2.3. Treatment of bis(β-acetoxyalkyl)ditellurides with acetic acid

Acetoxytelluration compounds are surely considered to be the intermediates in the diacetoxylation reaction which can be transformed into the corresponding *vic*-diacetates by direct S_N2 attack of an acetoxy group on a C–Te bond. Although such organotellurium compounds could not be isolated, *bis*(β-acetoxyalkyl)ditellurides were isolated after reduction. In order to confirm a conversion of a C–Te bond to a C–OAc bond [2], we carried out some experiments on the behavier of these compounds with acetic acid under conditions similar to the diacetoxylation reaction. Firstly, the treatment of *bis*(β-acetoxyalkyl)ditelluride **8** with acetic acid at reflux temperature for 5 h in the absence of TeO_2 and LiBr afforded the diacetate **3** (80% isolated yield) with a small amount of 4-vinylcyclohexene. From the compounds **9** and **10**, the corresponding *vic*-diacetates **5** and **6** were also formed respectively in high yields with a small amount of dienes (Scheme 6).



Scheme 5.



Scheme 6.

Secondly, compounds **8–10** were treated with the TeO_2/LiBr/AcOH system at reflux temperature for 5 h. In these cases the products were unidentified oily materials similar to those obtained in the direct diacetoxylation under severe conditions, only a very small amount of the corresponding *vic*-diacetates could be confirmed by GLC. These results clearly show that the diacetates **3**, **5** and **6**, initially produced, further reacted to give such oily materials, being consistent with those obtained by direct diacetoxylation of dienes.

3. Experimental details

^1H NMR spectra were recorded on a JEOL GSX-270 (270 MHz) spectrometer using Me_4Si as an internal standard in $CDCl_3$. ^{13} NMR spectra were recorded on JEOL FX-100 (25 MHz) and JEOL GSX-270 (67.8 MHz) spectrometers using Me_4Si as an internal standard in $CDCl_3$. IR spectra were measured with a Hitachi EPI-G2 spectrometer. GLC analyses were carried out with a Hitachi 163 instrument equipped with a EGSS-X (10% on Chromosorb W, 60-80 mesh, 3 mm × 2 m) column using nitrogen as the carrier gas. Commercially available organic and inorganic compounds were used without further purification. The isolation of pure products was carried out with column chromatography (SiO_2; *n*-hexane/ethyl acetate as eluent). 1-Phenylethyl acetate (**4**) was prepared by the acetylation of the corresponding commercial alcohol. *trans*-1,2-Diacetoxy-4-vinylcyclohexane and the compounds **5** and **6** were prepared separately by oxidation of the corresponding dienes with $(NH_4)_2S_2O_8$ and $FeSO_4 \cdot 7H_2O$ in acetic acid at 80°C for 5 h [12] and used as authentic samples for GLC and NMR analyses. Other products were isolated by column chromatography. A typical experimental procedure is given below.

3.1. Diacetoxylation of 4-vinylcyclohexene with TeO_2

The following example is a typical experimental procedure for the diacetoxylation of nonconjugated dienes.

A mixture of TeO_2 (1.59 g, 9.97 mmol), LiBr (0.863 g, 9.94 mmol), and acetic acid (60 ml) was heated with stirring under reflux for 2 h. To the resulting yellow–orange heterogeneous mixture was added 4-vinylcyclohexene (1.09 g, 10.0 mmol) and the mixture was stirred for 5 h under reflux, during which period the mixture gradually became a black suspension. The mixture was cooled and the solids were filtered off. The filtrate was treated with brine (200 ml) and then extracted with CH_2Cl_2 (3 × 60 ml). The extract was washed successively with aqueous $NaHCO_3$ and brine, and then dried over $MgSO_4$. Evaporation of the solvent left an oily residue. The residue was treated with acetic anhydride (3 ml) in pyridine (7 ml) at 80°C for 1 h to acetylate any free hydroxy groups. The resulting black homogeneous mixture was treated with brine (200 ml), made slightly acidic with aqeous HCl and then extracted with CH_2Cl_2 (3 × 60 ml). The extract was treated as described above and evaporation of the solvent left a dark orange oily residue. Column chromatography on SiO_2 afforded three fractions; (i) 1-phenylethyl acetate (**4**), (0.46 g, 28%) (elution with *n*-hexane : ethyl acetate (10 : 1)), (ii) a mixture of **2** and **3**, (0.91 g, 40%; **2** : **3** = 22 : 78) (*n*-hexane : ethyl acetate (5 : 1)) and (iii) an uncharacterized mixture (0.85 g) (ethyl acetate).

3.1.1. cis-1,2-Diacetoxy-cis-4-vinylcyclohexane (2)

^{1}H NMR: δ 1.47–1.64 (2H, m), 1.74–1.87 (4H, m), 2.05 (6H, s), 2.40 (1H, br s), 4.77–4.84 (2H, m), 4.97 (1H, dt, J = 10.6 and 1.5 Hz), 5.02 (1H, dt, J = 17.2 and 1.5 Hz), 5.74 (1H, ddd, J = 17.2, 10.6 and 5.9 Hz). ^{13}C NMR (67.8 MHz): δ 21.1 (q), 21.2 (q), 25.4 (t), 29.4 (t), 34.7 (t), 34.9 (d), 69.1 (d), 72.0 (d), 113.4 (t), 142.0 (d), 170.4 (s). IR (neat): ν 3040, 1740 (vs), 1640, 1250 (s), 1230 (vs), 1040 (s), 1020, 900 (s) cm^{-1}. Anal. for the mixture of **2** and **3**. Found: C, 63.51; H, 8.15. $C_{12}H_{18}O_4$ calcd.: C, 63.69; H, 8.02%.

3.1.2. trans-1,2-Diacetoxy-4-vinylcyclohexane

^{1}H NMR: δ 1.49–1.64 (2H, m), 1.74–1.87 (4H, m), 2.05 (6H, s), 2.40 (1H, br s), 4.85 (1H, dt, J = 5.9 and 3.7 Hz), 4.98 (1H, q, J = 5.1 Hz), 5.03 (1H, dt, J = 10.6 and 1.5 Hz), 5.08 (1H, dt, J = 17.2 and 1.5 Hz), 5.79 (1H, ddd, J = 17.2, 10.6 and 5.9 Hz). ^{13}C NMR (67.8 MHz): δ 21.1 (q), 25.5 (t), 26.4 (t), 32.0 (t), 35.2 (d), 69.6 (d), 70.4 (d), 113.7 (t), 141.8 (d), 169.9 (s), 170.0 (s). IR (neat): ν 3040, 1740 (vs), 1640, 1250 (s), 1230 (vs), 1040 (s), 1020, 900 (s) cm^{-1}. Anal. Found: C, 63.44; H, 7.89. $C_{12}H_{18}O_4$ calcd.: C, 63.69; H, 8.02%.

3.1.3. 4-(1,2-Diacetoxyethyl)-cyclohexene (3)

^{1}H NMR: δ 1.25–1.38 (1H, m), 1.77–2.05 (6H, m), 2.05 (3H, s), 2.06 (3H, s), 4.02 (2H, d, J = 5.5 Hz), 4.74–4.90 (1H, m), 5.64–5.69 (2H, m). ^{13}C NMR (67.8 MHz): δ 21.0 (q), 21.1 (q), 24.3 (t), 24.9 (t), 27.6 (t), 34.9 (d), 68.6 (d), 74.5 (d), 125.4 (d), 127.2 (d), 170.6 (s), 170.7 (s). IR (neat): ν 3040, 1740 (vs), 1640, 1250 (s), 1230 (vs), 1040 (s), 1020, 900 (s) cm^{-1}.

3.1.4. Compound 5

^{1}H NMR: δ 1.64–1.82 (2H, m), 2.06–2.13 (2H, m), 2.06 (6H, s), 4.04 (1H, ddd, J = 12.1, 6.2 and 2.6 Hz), 4.25 (1H, dt, J = 12.1 and 3.3 Hz), 4.98–5.13 (3H, m), 5.71–5.86 (1H, m). ^{13}C NMR (67.8 MHz): δ 20.8 (q), 21.0 (q), 29.4 (t), 29.9 (t), 65.0 (t), 71.0 (d), 115.5 (t), 137.4 (d), 170.5 (s), 170.7 (s). IR (neat): ν 3030, 1740 (vs), 1645, 1250 (s), 1240 (vs), 1040 (s), 1020 cm^{-1}. Anal. Found: C, 59.99; H, 8.29. $C_{10}H_{16}O_4$ calcd.: C, 59.97; H, 8.06%.

3.1.5. Compound 6

^{1}H NMR: δ 2.07 (3H, s), 2.10 (3H, s), 3.58 (2H, d, J = 5.1 Hz), 4.00 (2H, d, J = 5.5 Hz), 4.18 (1H, dd, J = 11.9 and 5.5 Hz), 4.34 (1H, dd, J = 11.9 and 3.7 Hz), 5.18–5.27 (3H, m), 5.89 (1H, ddt, J = 16.1, 9.2 and 5.5 Hz). ^{13}C NMR (67.8 MHz): δ 20.7 (q), 21.0 (q), 62.8 (t), 68.1 (t), 70.2 (d), 72.2 (t), 117.4 (t), 134.1 (d), 170.3 (s), 170.6 (s). IR (neat): ν 3040, 1740 (vs), 1640, 1250 (s), 1240 (vs), 1210, 1050, 1030, 1020 cm^{-1}. Anal. Found: C, 55.79; H, 7.31. $C_{10}H_{16}O_5$ calcd.: C, 55.53; H, 7.46%.

3.2. Isolation of acetoxytelluration compounds from nonconjugated dienes

The following example is a typical experimental procedure for the acetoxytelluration of nonconjugated dienes. A mixture of TeO_2 (1.60 g, 10.0 mmol), LiBr (0.871 g, 10.0 mmol), and acetic acid (60 ml) was stirred at 80°C for 2 h. To the resulting yellow–orange heterogeneous mixture was added 4-vinylcyclohexene (1.08 g, 9.98 mmol) and the mixture was heated at 80°C for 5 h with stirring. The mixture was cooled and the solids were filtered off. The filtrate was poured into aqueous $Na_2S_2O_3$, and the mixture was extracted with CH_2Cl_2 (3×60 ml), during which period the color of the extract changed from yellow to dark orange and elemental tellurium was deposited as a black precipitate. The extract was then treated in the same manner as for the diacetoxylation described above. Evaporation of the solvent left an orange solid and a dark-red oil. The orange solid was unstable in the air at room temperature and decomposed to a black solid in a few days. After dissolving all these residues in a very small amount of ethyl acetate, the solution was subjected to a column chromatography on SiO_2 to give an orange solid (0.62 g) (elution with *n*-hexane : ethyl acetate (10 : 1)) and *bis*(β-acetoxyalkyl)ditellurides **8** (1.79 g, 31%) (*n*-hexane : ethyl acetate (5 : 1)).

3.2.1. Compound 8

^{1}H NMR: δ 1.77–2.05 (14H, m), 2.06 (6H, s), 3.35–3.62 (4H, m), 4.76–4.90 (2H, m), 5.67 (4H, br s). ^{13}C NMR (67.8 MHz): δ 8.3 (t), 21.1 (q), 24.1 (t), 25.0 (t), 27.8 (t), 37.9 (d), 78.0 (d), 125.4 (d), 127.2 (d), 170.5 (s). IR (neat): ν 3020, 1745 (vs), 1645, 1250 (s), 1230 (vs), 1040 (s), 1020 cm^{-1}. Anal. Found: C, 41.00; H, 5.03. $C_{20}H_{30}O_4Te_2$ calcd.: C, 40.75; H, 5.09%.

3.2.2. Compound 9

^{1}H NMR: δ 1.73–1.82 (4H, m), 2.03–2.15 (4H, m), 2.05 (6H, s), 3.37–3.54 (4H, m), 4.88–5.07 (6H, m), 5.79 (2H, ddt, $J = 16.8$, 10.3 and 5.7 Hz). ^{13}C NMR (25 MHz): δ 10.0 (t), 21.2 (q), 29.5 (t), 34.0 (t), 74.8 (d), 115.2 (t), 137.4 (d), 170.3 (s). IR (neat) ν 3020, 1745 (vs), 1645, 1250 (s), 1230 (vs), 1040 (s), 1020 cm^{-1}. Anal. Found: C, 35.58; H, 4.88. $C_{16}H_{26}O_4Te_2$ calcd.: C, 35.75; H, 4.88%.

3.2.3. Compound 10

^{1}H NMR: δ 2.06 (6H, s), 3.41–3.88 (4H, m), 3.98–4.07 (4H, d, $J = 5.5$ Hz), 4.10–4.50 (4H, m), 5.02–5.33 (6H, m), 5.89 (2H, ddt, $J = 16.1$, 9.2 and 5.5 Hz). ^{13}C NMR (25 MHz): δ 13.0 (t), 21.1 (q), 62.9 (t), 68.1 (t), 70.9 (d), 117.4 (t), 134.2 (d), 170.5 (s). IR (neat): ν 3020, 1745 (vs), 1645, 1250 (s), 1230 (vs), 1040 (s), 1020 cm^{-1}. Anal. Found: C, 33.74; H, 4.60. $C_{16}H_{26}O_6Te_2$ calcd.: C, 33.85; H, 4.81%.

3.3. Treatment of bis(β-acetoxyalkyl)ditellurides with acetic acid

The following example is a typical experimental procedure for the conversion of *bis*(β-acetoxyalkyl)ditelluride into the corresponding *vic*-diacetate. A mixture of *bis*(β-acetoxyalkyl)ditelluride **8** (0.29 g, 0.50 mmol) and AcOH (6 ml) was stirred at reflux temperature for 5 h, during which period the color of the solution changed from dark-red to yellow–orange and elemental tellurium was deposited as a black precipitate. The reaction mixture was then worked up in the same manner as for the diacetoxylation. GLC analysis of the CH_2Cl_2 extract revealed the presence of the *vic*-diacetate **3** (80% isolated yield). Next, a mixture of **8** (0.29 g, 0.50 mmol), TeO_2 (0.080 g, 0.50 mmol), LiBr (0.043 g, 0.50 mmol), and AcOH (6 ml) was stirred at reflux temperature for 5 h, during which period the color of the solution changed from dark-red to yellow–orange and elemental tellurium was deposited as a black precipitate. The reaction mixture was then worked up in the same manner as for the diacetoxylation. The products were uncharacterized oily materials together with a very slight amount of **3** (by GLC).

References

[1] J. Bergman and L. Engman, *J. Organomet. Chem., 181* (1979) 335.
[2] S. Uemura, K. Ohe, S. Fukuzawa, S.R. Patil and N. Sugita, *J. Organomet. Chem., 316* (1986) 67.
[3] (a) S. Uemura, S. Fukuzawa and M. Okano, *Tetrahedron Lett.*, (1981) 5331; (b) S. Uemura, S. Fukuzawa, S.R. Patil and M. Okano, *J. Chem. Soc., Perkin Trans. 1*, (1985) 499.
[4] J. Bergman and L. Engman, *J. Am. Chem. Soc., 103* (1981) 5196.
[5] J. Bergman and L. Engman, *Tetrahedron Lett.*, (1979) 1509; *J. Organomet. Chem., 201* (1980) 377.
[6] J. Bergman and L. Engman, *Z. Naturforsch., Teil B, 35* (1980) 882.
[7] J. Bergman and L. Engman, *Tetrahedron Lett.*, (1978) 3279; *J. Org. Chem., 47* (1982) 5191.
[8] H. Suzuki, K. Ninomiya and M. Inouye, *Chem. Lett.*, (1985) 821.
[9] S. Fukuzawa, K.J. Irgolic and D.H. O'Brien, *Organometallics, 9* (1990) 3073.
[10] Yu.V. Migalina, I.M. Balog, V.G. Lendel, A.S. Koz'min and N.S. Zefirov, *Khim. Geterotsikl. Soedin*, (1978) 1212; *Chem. Abstr., 90* (1979) 6360x.
[11] M. Albeck and T. Tamary, *J. Organomet. Chem., 164* (1979) C23; *J. Organomet. Chem., 420* (1991) 35.
[12] W.E. Friestad and J.R. Peterson, *Tetrahedron Lett., 24* (1983) 4547; *Tetrahedron, 40* (1984) 1469.