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OXYTELLURATION OF OLEFINS TO (β-ALKOXY- AND β-HYDROXY-ALKYL)ARYLTELLURIUM DIHALIDES AND THEIR REACTIONS WITH REDUCING AGENTS AND AQUEOUS NaOH

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Summary

Treatment of olefinic hydrocarbons with phenyltellurium tribromide or a mixture of diphenylditelluride and bromine in alcohol affords (β-alkoxyalkyl)phenyltellurium dibromides in fair to good yield (alkoxytelluration of olefins). Various aryltellurium trichlorides, diphenylditelluride/$CuCl_2$, and phenyltellurocyanate/$CuCl_2$ can be used for the preparation of (β-alkoxyalkyl)aryltellurium dichlorides. Similar reactions in aqueous tetrahydrofuran or aqueous t-butyl alcohol result in the formation of the corresponding β-hydroxy compound (hydroxytelluration of olefins). The reaction is *trans* stereospecific in the cases of *cis*-2-butene and *cis*- and *trans*-4-octenes and regiospecific in the cases of all terminal olefins examined (1-hexene, 1-octene, 1-decene, styrene, α-methylstyrene, 2-methyl-1-pentene, and isobutylene), tellurium species attacking the terminal carbon solely. The diorganyltellurium dihalide produced is reduced to the corresponding diorganyltelluride by reducing agents such as N_2H_4, Na_2S, $Na_2S_2O_3$, and $NaHSO_4$ in aqueous solution. Treatment of the diorganyltellurium dibromide with aqueous NaOH affords either an allylic ether (by telluroxide elimination) or a telluroxide depending on the structure of the telluroxide.

Introduction

The known chemistry of organotellurium compounds is growing steadily from the viewpoint of organic synthesis [1]. One of the key reactions in this field is the introduction of tellurium into organic compounds. Oxytelluration of olefins seems to be an effective method for this purpose, since such functional groups as alkoxyl, hydroxyl, and acetoxyl can be introduced onto the neighboring position to the tellurium moiety simultaneously. To our knowledge, however, the method has so far been scarcely explored except the intramolecular lactonization of 2,2-diphenyl-4-pentenoic acid by an aryltellurium trichloride [2] and the intramolecular oxytelluration of some γ- and δ-hydroxy olefins by TeO_2/LiCl [3]. We have now found a new

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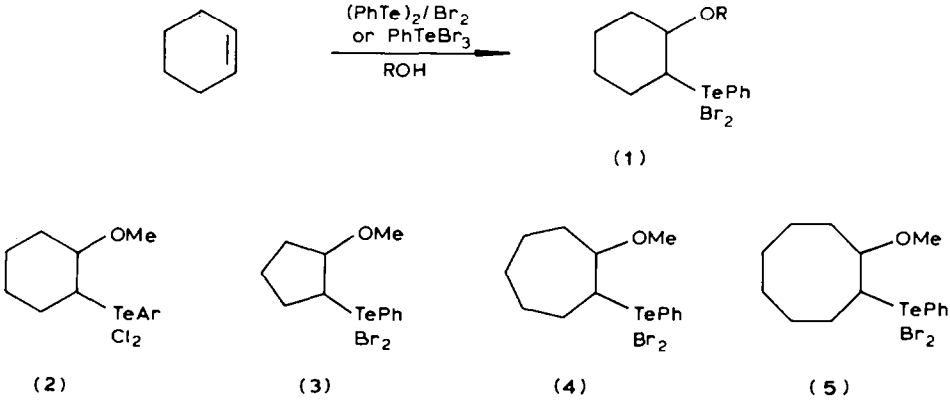
facile intermolecular oxytelluration reaction of olefins by various aryltellurium-(II) or -(IV) compounds in alcohol or aqueous solvent [4]. As one of our series of studies on organotellurium chemistry [5], we report here the details of this reaction together with some results of the treatment of the produced diorganyltellurium dihalides with reducing agents and aqueous NaOH.

Results and discussion

Oxytelluration of olefins

In a typical reaction, cyclohexene (1.2 equiv.) was added to a yellow homogeneous methanol solution of diphenylditelluride (1 equiv.) and bromine (3 equiv.) at room temperature, and the resulting solution was kept at 65°C for 1 h to give (2-methoxycyclohexyl)phenyltellurium dibromide (**1**; R = Me) as pale yellow crystals in 61% yield. The higher the concentration of the reactants and also the reaction temperature were, the higher the product yield was. The reaction proceeded even at room temperature, but at a slower rate. Since the reaction of diphenylditelluride with bromine is known to give phenyltellurium tribromide [6], the in situ formation of this compound followed by its attack is expected to occur during the reaction. In fact, we have confirmed that the same methoxytelluration reaction occurs using the latter reagent prepared separately (Scheme 1). The reaction proceeded equally well in ethanol and isopropanol as solvent, but the introduction of the t-butoxyl group did not occur in t-butyl alcohol. The hydroxytelluration of cyclohexene occurred in aqueous tetrahydrofuran or t-butyl alcohol to afford (**1**; R = H), while its acetoxytelluration in $CHCl_3$/AcOH (5/1) solvent failed and over 80% of phenyltellurium(IV) tribromide was recovered after stirring the mixture for 2 h at refluxing temperature. Other organotellurium compounds such as *p*-tolyl- and *p*-methoxyphenyl-tellurium trichlorides and phenyltellurocyanate can be used for this alkoxytelluration to give **2**, while the addition of a tellurium species did not occur in the case of phenyltellurium triiodide. Attempts to improve the yield of **1** (R = Me) by the addition of several acids or metal halides resulted only in low yields [7]. Typical results are summarized in Table 1.

From other cyclic olefins such as cyclopentene, cycloheptene, and cyclooctene, the corresponding methoxytelluration products (**3**–**5**) were obtained in fair yields by



SCHEME

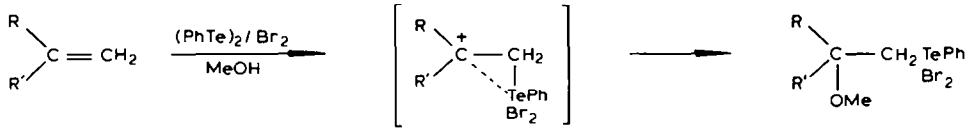
TABLE 1

OXYTELLURATION OF CYCLOHEXENE UNDER VARIOUS CONDITIONS

Cyclohexene (mmol)	Te reagent (mmol)		Solvent (ml)		Reaction temp. (°C)	Reaction time (h)	Product and yield (%) [a]	
5	$(PhTe)_2/Br_2$	2.5/7.5	MeOH	20	65	1	**1** (R = Me)	44
5	$(PhTe)_2/Br_2$	2.5/7.5	MeOH	20	65	3	**1** (R = Me)	52
6	$(PhTe)_2/Br_2$	2.5/7.5	MeOH	10	65	1	**1** (R = Me)	50
6	$(PhTe)_2/Br_2$	2.5/7.5	MeOH	5	65	1	**1** (R = Me)	61
6	$(PhTe)_2/Br_2$	2.5/7.5	MeOH	5	100 [b]	1	**1** (R = Me)	77
6	$(PhTe)_2/Br_2$	2.5/7.5	MeOH	5	25	24	**1** (R = Me)	61
6	$PhTeBr_3$	5	MeOH	10	65	1	**1** (R = Me)	65
6	$PhTeBr_3$	5	EtOH	5	78	1	**1** (R = Et)	48
6	$PhTeBr_3$	5	Pr^iOH	5	82	1	**1** (R = Pr^i)	35
6	$PhTeBr_3$	5	Bu^tOH/H_2O	5	82	1	**1** (R = H)	50
6	$PhTeBr_3$	5	THF/H_2O	5	67	1	**1** (R = H)	50
6	$PhTeCl_3$	5	MeOH	5	65	1	**2** (Ar = Ph)	62
6	$p\text{-}MeC_6H_4TeCl_4$	5	MeOH	5	65	1	**2** (Ar = $p\text{-}MeC_6H_4$)	60
4	$p\text{-}MeOC_6H_4TeCl_3$	2	MeOH	5	65	1	**2** (Ar = $p\text{-}MeOC_6H_4$)	65
8	$PhTeCN/CuCl_2$	4/24	MeOH	5	65	1	**2** (Ar = Ph)	62
4	$(PhTe)_2/CuCl_2$	1/6	MeOH	5	65	1	**2** (Ar = Ph)	69

[a] Isolated yield; based on Te reagent. [b] Carried out in a glass pressure bottle.

using the $(PhTe)_2/Br_2$ system. Application to several terminal olefins such as 1-hexene, 1-octene, 1-decene, styrene, α-methylstyrene, 2-methyl-1-pentene, and isobutylene afforded the corresponding (2-methoxyalkyl)phenyltellurium dibromide (**6**) almost solely in any case (Scheme 2). The ^{13}C NMR spectrum of the crude



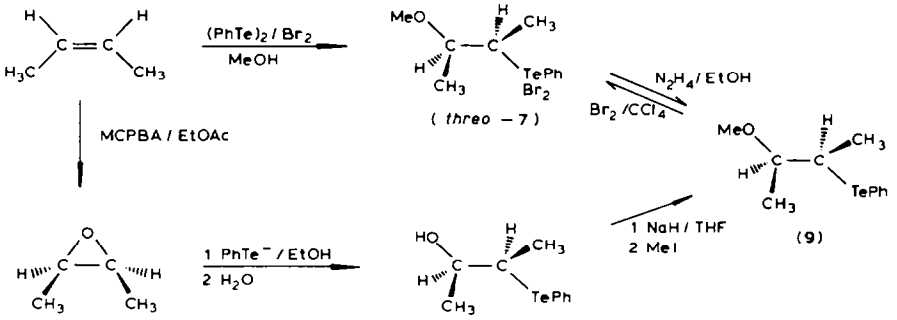
(A) (6)

(7) (8)

SCHEME 2

product and also of the corresponding telluride obtained by reduction (vide infra) did not show any signals due to the regioisomer of **6**, and furthermore GLC analysis of the telluride showed only one peak. This completely regiospecific addition where tellurium attacks only the terminal carbon seems to be characteristic of this alkoxytelluration reaction, since the addition of the species X^+Y^- to a terminal olefin usually gives a regioisomeric mixture of Markovnikov and anti-Markovnikov addition products [8]. Thus, in the case of the closely related oxyselenation and amidoselenation of terminal olefins, the corresponding regioisomer produced by attack of the Se species at the penultimate carbon was always formed in a 10–20% yield compared to the major isomer [9,10,11]. The reason for this specificity seems to be due to the bulkiness of the $PhTeBr_2^+$ or $PhTeBr_3$ species, which favors attack on the less hindered terminal carbon to give the intermediate **A**. In fact, the product yields in the alkoxytelluration of internal olefins such as 2-butenes and 4-octenes (**7** and **8**, respectively) were always lower than those from monosubstituted terminal olefins under the same reaction conditions. Furthermore, 2,2-disubstituted terminal olefins react more slowly than monosubstituted ones; i.e., styrene vs. α-methylstyrene, and 1-hexene vs. 2-methyl-1-pentene. This fact suggests that steric factors play a more important role than electronic factors in this alkoxytelluration reaction.

The stereochemical course of this reaction has been investigated using *cis*- and *trans*-2-butenes and *cis*- and *trans*-4-octenes as starting substrates. From the reaction of *cis*-2-butene at 100°C for 1 h in a glass pressure bottle, 3-methoxy-2-butylphenyltellurium dibromide (**7**) was obtained in 46% yield. This compound was prepared separately from *cis*-2-butene via several steps such as epoxidation, ring-opening by phenyltelluroate ion, methylation, and bromination as shown in Scheme 3, and thus was revealed to be the *threo* isomer: m.p., ^1H NMR, and the retention time of the telluride (**9**) are completely consistent with each other, and a mixed melting point showed no depression. Similarly, the *erythro* isomer of **7** was obtained from *trans*-2-butene, but this was slightly contaminated with the *threo* isomer (*erythro*: *threo* = 80–85 : 15–20 by ^1H NMR of the dibromide and by GLC of the telluride obtained



SCHEME 3

by reduction). The isomer ratio hardly depended on the reaction temperature (20–100°C) and the reaction time (1–24 h), the fact showing that the *threo*-isomer is not formed by an isomerization of the initially formed *erythro*-isomer [12]. From *cis*- and *trans*-4-octenes, on the other hand, only the corresponding isomers of **8** were obtained. The isomer from *cis*-4-octene was revealed to be *threo*-**8** [J(H(4)–H(5)) = 10 Hz] by comparing the vicinal coupling constant of the two methine protons in the ^{1}H NMR spectrum with that in *threo*-**7** [J(H(2)–H(3)) = 10 Hz]. The comparison of the ^{13}C chemical shifts of C-Te(Br_2)Ph in **7** (70.4 ppm for *threo*- and 64.1 ppm for *erythro*-) with those in **8** also shows that *threo*-**8** (74.1 ppm) and *erythro*-**8** (69.5 ppm)

(Continued on p. 211)

TABLE 2

ALKOXYTELLURATION OF VARIOUS OLEFINS [a]

Olefin (6 mmol)	Reaction temp. (°C)	Reaction time (h)	Product and yield	(%) [b]
Cyclopentene	65	1	**3**	52
Cyclohexene	65	1	**1** (R = Me)	61
Cycloheptene	65	1	**4**	52
Cyclooctene [c]	65	5	**5**	42
1-Hexene	65	1	**6** (R = Bu, R′ = H)	63
1-Octene	65	1	**6** (R = Hexyl, R′ = H)	70
1-Decene	65	1	**6** (R = Octyl, R′ = H)	66
Styrene	65	1	**6** (R = Ph, R′ = H)	58
α-Methylstyrene	65	1	**6** (R = Ph, R′ = Me)	36
2-Methyl-1-pentene	65	1	**6** (R = Pr, R′ = Me)	36
Isobutylene [d,e]	100	1	**6** (R = R′ = Me)	50
cis-2-Butene [d,e]	20	24	*threo*-**7**	46
cis-2-Butene [d,e]	100	1	*threo*-**7**	46
trans-2-Butene [d,e]	20	24	*erythro*-**7** [f]	10
trans-2-Butene [d,e]	100	1	*erythro*-**7** [f]	44
trans-2-Butene [d,e]	100	24	*erythro*-**7** [f]	66
cis-4-Octene	65	5	*threo*-**8**	44
trans-4-Octene	65	5	*erythro*-**8**	28
trans-4-Octene [e]	100	10	*erythro*-**8**	43

[a] $(PhTe)_2$ 2.5 mmol, Br_2 7.5 mmol, and MeOH(5 ml). [b] Isolated yield; based on Te reagent. [c] 8 mmol. [d] Olefins were used in a large excess (~ 25 mmol). [e] Carried out in a glass pressure bottle. [f] A mixture of *erythro*- (82 ~ 84%) and *threo*- (16 ~ 18%) isomers.

TABLE 3

CHARACTERIZATION OF ALKOXYTELLURATION PRODUCTS, (2-ALKOXYALKYL)ARYLTELLURIUM DIHALIDES

Compound	m.p.(°C)	Chemical Shifts δ(ppm)(J,Hz)		Found(Calcd.)	
		^{1}H NMR [a]	^{13}C NMR [b]	%C	%H
1 (R = Me)	169–171	1.0–1.5(m, 2H), 1.5–2.1(m, 4H), 2.2–2.55(m, 2H), 3.46 (s, 3H), 3.7–4.4(m, 2H), 7.2–7.6(m, 3H), 8.1–8.4 (m, 2H)	23.4(t), 27.5(t), 27.5(t), 31.7(t), 56.3(q), 71.5(d, *C*–Te), 79.1(d), 124.1(s), 129.3(d), 130.8(d), 136.1 (d)	32.54 (32.69)	3.55 (3.80)
2 (Ar = *p*-MeC_6H_4)	110–111	1.0–1.2(m, 8H), 2.31(s, 3H), 3.45(s, 3H), 3.7–4.2(m, 2H), 7.24(d, 2H, *J* = 8), 8.04(d, 2H, *J* = 8)		41.54 (41.74)	4.97 (5.00)
2 (Ar = *p*-$MeOC_6H_4$)	126–127	0.95–2.6(m, 8H), 3.45(s, 3H), 3.70(s, 3H), 3.5–4.0 (m, 2H), 6.94(d, 2H, *J* = 9) 8.04(d, 2H, *J* = 9)		39.58 (40.15)	4.87 (4.81)
2 (Ar = Ph)	180–182	1.0–2.5(m, 8H), 3.50(s, 3H), 3.7–4.2(m, 2H), 7.4–7.7(m, 3H), 8.1–8.4(m, 2H)		40.02 (40.14)	4.81 (4.63)
3	106–107	1.5–2.0(m, 4H), 2.0–2.6(m, 2H), 3.22(s, 3H), 4.2–4.6 (m, 2H), 7.3–7.55(m, 3H), 8.1–8.3(m, 2H)		31.08 (31.09)	3.20 (3.48)
4	154–155	1.2–1.8(m, 6H), 1.8–2.5(m, 4H), 3.50(s, 3H), 3.6–4.7 (m, 2H), 7.3–7.6(m, 3H), 8.1–8.4(m, 2H)		33.91 (34.20)	3.83 (4.10)
5	147–148	1.2–2.3(m, 12H), 3.45(s, 3H), 3.6–4.1(m, 1H), 4.3–4.8(m, 1H), 7.2–7.6(m, 3H), 7.9–8.3(m, 2H)		35.44 (35.62)	4.35 (4.39)
1 (R = Et)	140.5–141	1.0–2.5(m, 8H), 1.30(t, 3H), 3.2–4.4(m, 4H), 7.3–7.65(m, 3H), 8.05–8.5(m, 2H)		33.90 (34.20)	4.17 (4.10)

1 (R = Pr^i)	144–146	1.0–2.4(m, 8H), 1.20(d, 6H), 3.2–4.3(m, 3H), 7.3–7.7(m, 3H), 8.0–8.3(m, 2H)		35.24 (35.62)	4.44 (4.39)
6 (R = Bu, R′ = H)	oil	0.8–1.0(t, 3H), 1.2–1.5(m, 4H), 1.5–2.0(m, 2H), 3.50 (s, 3H), 3.95–4.3(m, 3H), 7.4–7.6(m, 3H), 8.05–8.3 (m, 2H)	13.9(q), 22.7(t), 26.4(t), 32.2(t), 57.2(t, *C*–Te), 57.4(q), 75.4(d), 128.6 (s), 129.7(d), 131.1(d), 134.5(d)	32.70 (32.55)	4.36 (4.20)
6 (R = Hexyl, R′ = H)	oil	0.86(t, 3H), 0.8–2.0(m, 10H), 3.45(s, 3H), 3.85–4.2(m, 3H), 7.2–7.5(m, 3H), 7.8–8.2(m, 2H)	13.9(q), 22.3(t), 24.2(t), 29.1(t), 31.4(t), 32.5(t), 56.9(t, *C*–Te), 57.2(q), 75.3(d), 128.6(s), 129.5 (d), 130.9(d), 134.4(d)	35.79 (35.48)	5.05 (4.76)
6 (R = Octyl, R′ = H)	oil	0.6–2.1(m, 17H), 3.46(s, 3H), 3.5–4.2(m, 3H), 7.3–7.6(m, 3H), 7.9–8.2(m, 2H)	14.0(q), 22.5(t), 24.4(t), 29.0(t), 29.3(t), 29.6(t), 31.7(t), 32.7(t), 57.4(t, *C*–Te), 57.4(q), 75.5(d), 128.7(s), 131.1(d), 134.4 (d), 136.1(d)	38.01 (38.11)	5.54 (5.27)
6 (R = Ph, R′ = H)	121–122	3.20(s, 3H), 3.95(d, 2H, J = 8), 5.0(t, 1H, J = 8), 7.1–7.5(m, 8H), 7.85–8.2(m, 2H)		35.73 (36.05)	3.32 (3.23)
6 (R = Ph, R′ = Me)	129–130	2.10(s, 3H), 3.22(s, 3H), 4.33(d, 1H, J = 11), 4.62(d, 1H, J = 11), 7.3–7.7(m, 8H), 7.9–8.15(m, 2H)	23.6(q), 51.8(q), 64.4(t, *C*–Te), 78,2(s), 126.6(d), 128.2(d), 128.9(d), 129.7 (d), 130.4(s), 131.0(d), 134.1(d), 142.6(s)	37.21 (37.41)	3.57 (3.53)
6 (R = Pr, R′ = Me)	59–60	0.75–2.0(m, 7H), 1.54(s, 3H), 3.33(s, 3H), 4.10(d, 1H, J = 11), 4.45(d, 1H, J = 11), 7.15–7.5(m, 3H), 7.8–8.1(m, 2H)		32.14 (32.55)	4.23 (4.18)
6 (R = R′ = Me)	96–97	1.50(s, 6H), 3.35(s, 3H), 4.13(s, 2H), 7.2–7.6(m, 3H) 7.85–8.25(m, 2H)		28.74 (29.25)	3.60 (3.57)
threo-**7**	138–139	1.33(d, 3H, J = 6), 1.64(d, 3H, J = 7), 3.45(s, 3H), 3.86 dq, 1H, J = 10, 6), 4.34(dq, 1H, J = 10, 7), 7.3–7.5(m, 3H), 8.1–8.3(m, 2H)	13.8(q), 16.7(q), 57.0(q), 70.4(d, *C*–Te), 77.7(d), 125.7(s), 129.5(d), 131.0(d), 136.5(d)	29.28 (29.25)	3.44 (3.57)

(to be continued)

TABLE 3 (continued)

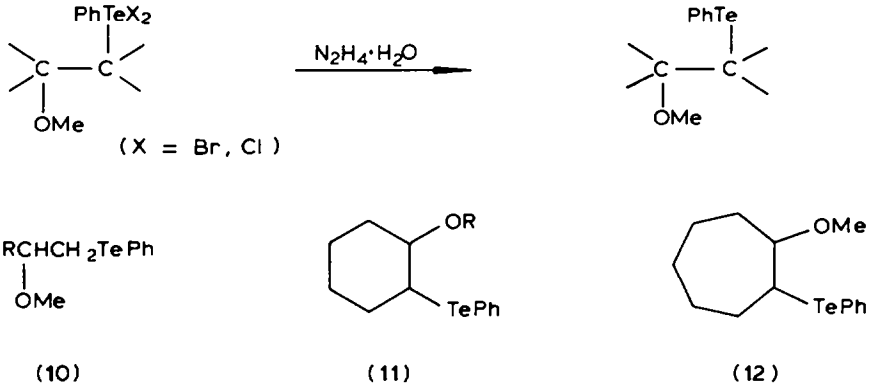
Compound	m.p.(°C)	Chemical Shifts δ(ppm)(J,Hz)		Found(Calcd.)	
		^{1}H NMR [a]	^{13}C NMR [b]	%C	%H
erythro-**7** [c]	110 -111	1.34(d, 3H, J = 6), 1.72(d, 3H, J = 8), 3.46(s, 3H), 4.1–4.5(m, 2H), 7.3–7.5(m, 3H), 8.0–8.3(m, 2H)	13.8(q), 15.8(q), 57.0(q), 64.1(d, *C*-Te), 75.5(d), 127.3(s), 129.8(d), 131.2(d), 134.6(d)	29.02 (29.25)	3.59 (3.57)
threo-**8**	107 -108	0.70(t, 3H, J = 7), 0.98(t, 3H, J = 7), 1.0–2.35(m, 8H), 3.50(s, 3H), 3.88(dt, 1H, J = 10, 4), 4.43(ddd, 1H, J = 10, 6, 5), 7.4–7.6(m, 3H), 8.25–8.45(m, 2H)	13.6(q), 14.3(q), 16.6(t), 23.0(t), 32.2(t), 32.7(t), 58.0(q), 74.1(d, *C*-Te), 81.3(d), 125.6(s), 131.1 (d), 136.0(d), 136.4(d)	35.17 (35.48)	4.82 (4.76)
erythro-**8**	62 - 63	0.84(t, 3H, J = 7), 1.00(t, 3H, J = 7), 1.1–2.3(m, 8H), 3.50(s, 3H), 3.9–4.15(m, 1H), 4.3–4.65(m, 1H), 7.3–7.6(m, 3H), 7.9–8.2(m, 2H)	13.7(q), 14.0(q), 19.1(t) 22.8(t), 30.7(t), 34.1(t), 59.0(q), 69.5(d, *C*-Te), 81.3(d), 128.2(s), 129.6 (d), 131.1(d), 135.3(d)	35.23 (35.48)	4.89 (4.76)
1 (R = H)	104 -105	1.0–2.4(m, 8H), 2.9(br s, 1H, OH), 4.0–4.4(br, 2H), 7.3–7.6 (m, 3H), 8.0–8.4(m, 2H)		31.14 (31.08)	3.60 (3.48)

[a] 60 MHz NMR data except in the cases of **1** (R = Me), **3**, **6** (R = Bu, R′ = Me), *threo*- and *erythro*-**7**, and *threo*- and *erythro*-**8** [100 MHz NMR]. [b] *C*-Te denotes alkyl *C*-Te. [c] Contains ca. 15% of *erythro*-**7**.

are formed from *cis*- and *trans*-4-octenes, respectively. These results show that phenyltellurium species and the methoxy group add to the olefin in a *trans* fashion completely in the cases of *cis*-2-butene and *cis*- and *trans*-4-octenes, and preferentially in the case of *trans*-2-butene. Typical results are shown in Table 2. Characterization of new alkoxytelluration products is summarized in Table 3.

Treatment of oxytelluration products with reducing agents and aqueous NaOH

Although diorganyltellurium dichlorides can be reduced to diorganyltellurides by various reducing agents [13], the chlorotelluration products of olefins such as bis(2-chloropropyl)tellurium dichloride [14] and 2-chloro-5-cyclooctenyltellurium dichloride [15] generate the parent olefins and elemental tellurium upon similar treatment. In sharp contrast to the case of the chlorotelluration of olefins it was found that the oxytelluration products of olefins **1**–**8** were readily reduced to the corresponding tellurides quantitatively, as in the case of normal diorganyltellurium dihalides, by N_2H_4, Na_2S, $Na_2S_2O_3$ or $NaHSO_4$ in aqueous solution (Scheme 4). It is also known that dialkyltellurium dichlorides prepared by the intramolecular oxytelluration of some hydroxyolefins were reduced to their corresponding tellurides by using $Na_2S_2O_5$ or $N_2H_4 \cdot H_2O$ [3]. All the tellurides are yellow oils which were oxidized slowly on standing in air and were kept unchanged for a long time under N_2 in the dark. ^1H and ^{13}C NMR data of some of them (**10**–**12**) are shown in

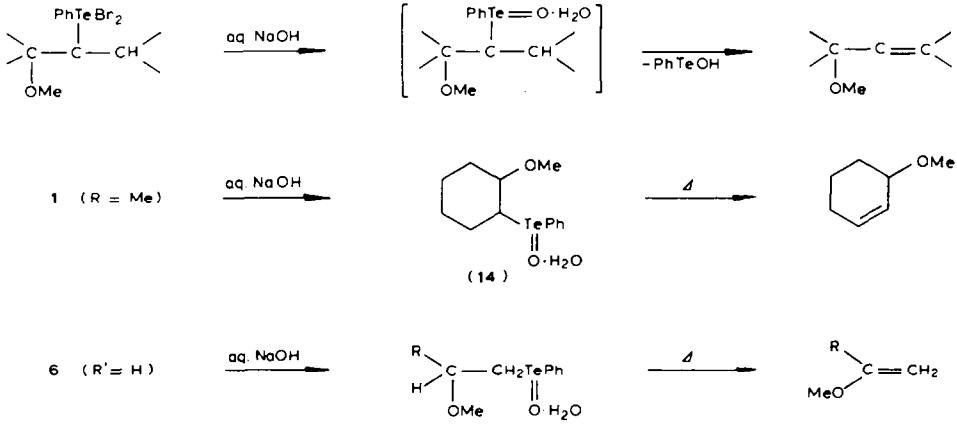


(10) (11) (12)

SCHEME 4

Table 4 for comparison with the corresponding dibromides. In the ^1H NMR spectrum a ca. 0.5–1 ppm high-field shift was observed for the hydrogen on the carbon bearing the tellurium moiety by changing the moiety from $PhTeBr_2$ to PhTe, while in the ^{13}C NMR spectrum ca. 40–43 ppm and ca. 13–17 ppm high field shifts occurred for alkyl *C*–Te and phenyl *C*–Te, respectively, by such replacement.

Treatment of an alkoxytelluration product with aqueous NaOH at room temperature afforded either an allylic ether (by telluroxide elimination) or a telluroxide monohydrate depending on the structure of the telluroxide. Thus, from sec-alkylphenyltellurium dibromides such as **4**, **5** and **8** the corresponding allylic ethers were readily obtained in high yields, while in the cyclohexyl and primary alkyl cases such as **1** and **6** the corresponding telluroxides were isolated as stable compounds which afford similar elimination products, including vinylic ethers, only by neat pyrolysis at temperatures above 200°C (Scheme 5) [16].



SCHEME 5

TABLE 4

^{1}H AND ^{13}C NMR DATA OF SOME DIORGANYLTELLURIDES

Diorganyl telluride	Chemical Shifts δ (ppm) (*J*, Hz)	
	^{1}H NMR [a]	^{13}C NMR [b]
11 (R = Me)	1.0–2.4(m, 8H), 3.32(s, 3H), 3.1–3.8(m, 2H), 7.0–7.4(m, 3H), 7.7–7.9 (m, 2H)	23.8(t), 27.5(t), 31.3(t), 31.8(d, *C*–Te), 33.6(t), 56.0(q), 84.3(d), 111.1(s) 127.7(d), 128.7(d), 140.8(d)
10 (R = Bu)	0.85(t, 3H), 1.0–1.8(m, 6H), 2.9–3.5(m, 3H), 3.22(s, 3H), 7.0–7.3(m, 3H), 7.55–7.8(m, 2H)	13.9(q), 14.5(t, *C*–Te), 22.6(t), 27.3(t), 34.6(t), 56.3(q), 80.8(d), 111.8 (s), 127.0(d), 128.6(d), 138.0(d)
10 (R = Octyl)	0.87(t, 3H), 0.8–1.9(m, 14H), 3.27(s, 3H), 2.75–3.7(m, 3H), 6.95–7.25(m, 3H), 7.4–7.7(m, 2H)	14.0(q), 14.5(t, *C*–Te), 22.6(t), 25.2(t), 29.1(t), 29.4(t), 29.5(t), 31.8(t), 34.9(t), 56.3(q), 80.9(d), 111.8(s), 127.0(d), 128.6 (d), 138.0(d)
10 (R = Ph)	3.16(s, 3H), 2.6–3.85(m, 2H), 4.40(dd, 1H, *J* = 6, 8), 7.0–7.4(m, 8H), 7.5–7.7 (m, 2H)	
11 (R = Et)	1.0–2.3(m, 8H), 1.18(t, 3H), 3.05–3.9(m, 4H), 7.0–7.3(m, 3H), 7.6–7.9 (m, 2H)	15.6(q), 24.1(t), 27.6(t), 32.5(t), 32.5(d, *C*–Te), 33.9(t), 64.1(t), 83.1(d), 111.7(s), 127.7(d), 128.8(d), 140.9(d)
12	1.0–2.2(m, 10H), 3.19(s, 3H), 3.2–4.0(m, 2H), 6.9–7.3(m, 3H), 7.5–7.8 (m, 2H)	22.0(t), 27.6(t), 28.3(t), 31.2(t), 32.4(t), 35.2(d, *C*–Te), 56.4(q), 87.2(d), 113.0(s), 127.7(d), 128.8 (d),*β*140.4(d)
11 (R = H)	1.0–2.3(m, 8H), 2.6(br s, 1H, OH), 3.1–3.4(br, 2H), 7.0–7.3(m, 3H), 7.6–7.9(m, 2H)	

[a] 60 MHz NMR data except in case of **11** (R = Me)[100 MHz NMR]. [b] *C*–Te denotes alkyl *C*–Te.

Experimental

^1H NMR spectra were recorded with JEOL JNM FX-100(100 MHz) and Varian EM-360(60 MHz) instruments on solutions in $CDCl_3$, with Me_4Si as an internal standard. ^{13}C NMR spectra were taken at 25.1 MHz with a JEOLCO ^{13}C Fourier transform NMR system and were recorded on solutions in $CDCl_3$, after 250–1000 pulses with intervals of 2.7–2.8 s. GLC analyses were carried out using a Shimadzu 4CMPF apparatus using Silicone QF-1(5%)-Chromosorb-W (1 m), PEG 6000(25%)-Shimalite (1 m), and EGSS-X(3%)-Chromosorb-W (1 and 3 m) columns (N_2 as carrier gas). For analysis of *cis*- and *trans*-2-butenes a Durapak (n-octane/Porasil C) (2 m) column was used (Yanagimoto G8 apparatus at 25°C, He as carrier gas). Melting points were determined with a Shimadzu MM-2 micro melting point determination apparatus and were uncorrected. Commercially available Te and $TeCl_4$ (Nakarai Chemicals) and Mg turnings (Wako Pure Chemical) were used without further purification, while commercial organic compounds were distilled immediately before use. Diphenylditelluride [17], phenyltellurium tribromide and triiodide [6], aryltellurium trichlorides [18,19], and phenyltellurocyanate [20] were prepared as reported previously.

Methoxytelluration of cyclohexene to (2-methoxycyclohexyl)phenyltellurium dibromide (1; R = Me)

In a 30-ml round-bottomed flask equipped with a condensor, a dropping funnel, and a magnetic stir bar, a methanol (3 ml) solution of diphenylditelluride (1.02 g, 2.5 mmol) and then a methanol (2 ml) solution of bromine (1.20 g, 7.5 mmol) were added at 0°C. On stirring for 30 min at room temperature a yellow homogeneous solution was obtained to which cyclohexene (0.49 g, 6.0 mmol) was added. The resulting solution was stirred at reflux for 1 h, during which period a yellow solid appeared as a precipitate. After cooling, the precipitated pale yellow solid (**1**; R = Me) was collected by filtration, washed with a small amount of methanol, and dried in vacuo (1.45 g, 3.0 mmol, 61%). To obtain an analytically pure compound it was recrystallized from methanol-chloroform or hexane-chloroform.

Methoxytelluration of cis-2-butene to threo-2-(3-methoxybutyl)phenyltellurium dibromide (7)

A solution of diphenyl ditelluride (1.02 g, 2.5 mmol) and bromine (1.20 g, 7.5 mmol) in methanol (5 ml) was placed in a 50-ml glass pressure bottle (Taiatsu Glass Industry Co. Ltd.). *cis*-2-Butene (2.2 ml, ca. 25 mmol) was charged at −78°C, and after the temperature had been raised to 100°C the solution was stirred under pressure for 1 h using a magnetic stirrer. After cooling, the resulting yellow solid (**7**) was collected by filtration (1.04 g, 2.30 mmol, 46%). ^1H and ^{13}C NMR analysis of this crude product and also GLC analysis of the corresponding diorganyltelluride obtained by reduction with $N_2H_4 \cdot H_2O$ revealed that it consisted of only one isomer, *threo*-**7**.

Treatment of 1 (R = Me) with $N_2H_4 \cdot H_2O$ to give 2-methoxycyclohexyl phenyl telluride (11; R = Me)

To a heterogeneous ethanol (20 ml) solution of **1** (R = Me) (2.40 g, 5.0 mmol) was added hydrazine hydrate ($N_2H_4 \cdot H_2O$, 2.5 g, 50 mmol) drop by drop at room

temperature with stirring [18]. The resulting pale yellow homogeneous solution was added with brine (150 ml) and extracted with diethyl ether (3 × 50 ml), and the extract was dried over $MgSO_4$. Evaporation of solvent left a yellow oil which was subjected to column chromatography (silica gel, Wakogel C-200) [hexane-ethyl acetate (10 : 1–5 : 1) as eluent] to give a yellow oil of pure **11** (R = Me) (1.60 g, 5.0 mmol, 100%).

A similar procedure was applied in the case of the reduction with aqueous Na_2S, $Na_2S_2O_3$ or $NaHSO_4$.

Preparation of an authentic sample of threo-7

threo-3-(Phenyltelluro)-2-butanol (yellow oil, 2.08 g, 7.5 mmol, 75%) was prepared by the epoxidation of *cis*-2-butene (2.2 ml, ca. 25 mmol) using 80% *m*-chloroperbenzoic acid (2.15 g, 10 mmol) at 20°C for 2 h in ethyl acetate (10 ml) in a 50-ml glass pressure bottle followed by *trans* ring-opening of the epoxide by phenyltelluroate anion using $(PhTe)_2$(2.04 g, 5 mmol) and $NaBH_4$(0.76 g, 20 mmol) in ethanol (50 ml) at 0–20°C for 10 h [21]. Methylation of the alcohol (1.1 g, 4 mmol) with methyl iodide (4.5 g, 32 mmol) and sodium hydride (0.29 g, 6 mmol) in THF (20 ml) at 20°C for 16 h [22] afforded *threo*-2-(3-methoxybutyl)phenyl telluride (**9**) (0.18 g, 0.62 mmol, 15%) [60MHz ^{1}H NMR δ(ppm) 1.22(d, 3H, J = 6), 1.55(d, 3H, J = 6), 3.30(s, 3H), 3.1–3.8(m, 2H), 7.0–7.35(m, 3H), 7.65–8.0(m, 2H)] which gave *threo*-**7** quantitatively by treatment with Br_2 (0.1 g, 0.62 mmol) in $CHCl_3$ at 20°C.

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epoxidation also resulted in a formation of a mixture of *erythro*- and *threo*-7 at an isomer ratio (ca. 85 : 15) similar to that from the direct methoxytelluration. The reason for the slight formation of *threo*-isomer is not yet known.

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