

α -ELIMINATION OF ORGANIC HALIDES FROM ORGANOTELLURIUM(IV) HALIDES

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Summary

Three types of α -elimination (oxidative, photolytic, and thermal) of organotellurium(IV) halides to give organic halides have been disclosed. Treatment of organotellurium(IV) halides with some oxidants, preferably *t*-butyl hydroperoxide, in 1,4-dioxane, acetic acid, or acetonitrile affords the corresponding organic halides in good yields with retention of configuration and by *ipso*-replacement. The reactivity order of this α -elimination is roughly as follows: alkyl > aryl > alkenyl. The main reaction course seems to be a 1,2-tellurium halogen shift in unstable organotellurium(VI) compounds formed in situ by oxidation. Similar α -elimination also occurs by photolysis of these compounds with a high-pressure mercury lamp in benzene as the solvent. Here, a cross-coupling of the organic moiety with benzene scarcely occurs except for the cases of diaryltellurium(IV) dihalides. Neat pyrolysis of some alkyl(phenyl)tellurium(IV) dibromides at 200–250 °C (Kugelrohr distillation apparatus) again results in α -elimination to produce the corresponding alkyl bromides almost quantitatively.

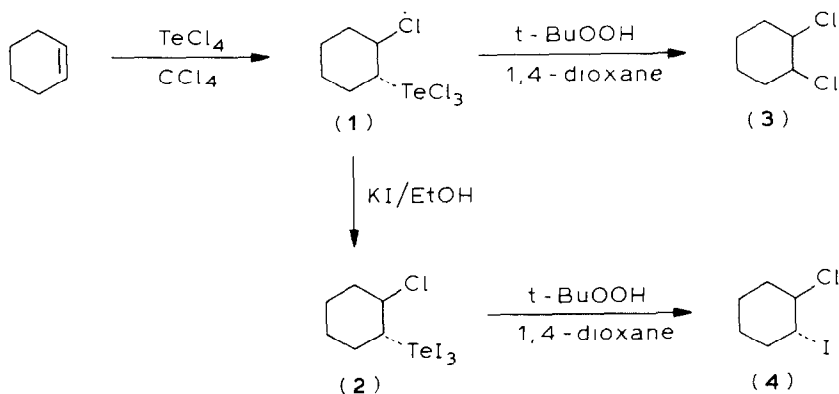
Introduction

The utility of organotellurium compounds for organic synthesis is increasing [1] where the conversion of a tellurium moiety to other functional groups is one of the important subjects. It has been reported previously that a carbon–tellurium bond can be transformed into a carbon–halogen bond in reactions of some aryltellurium(IV) compounds [2] and vinyltellurium(IV) chlorides [3] with molecular halogens. We now find that a new type of carbon–tellurium bond fission occurs in organotellurium(IV) halides themselves to give the corresponding organic halides when they are treated with peroxide, irradiated with a high-pressure mercury lamp, or heated. The characteristic nature of these reactions is an *ipso*-replacement of the tellurium moiety by the halogen bound to the tellurium atom, and the process may be considered a 1,2-tellurium halogen shift in all cases. We describe here the details of these reactions [4].

Results and discussion

Oxidative α -elimination reaction

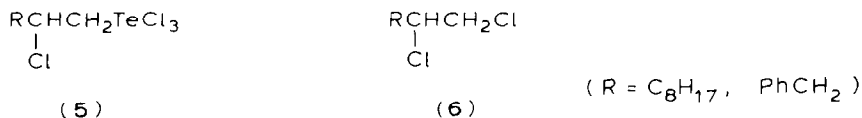
When a homogeneous solution of *trans*-2-chlorocyclohexyltellurium trichloride (**1**) [5,6] and *t*-butyl hydroperoxide (*t*-BuOOH) in 1,4-dioxane was stirred at reflux for 30 min, 1,2-dichlorocyclohexane (**3**) was formed in over 90% yield (Scheme 1). The



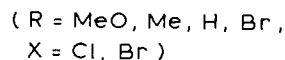
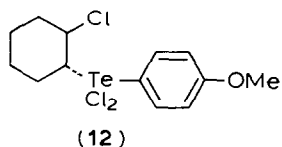
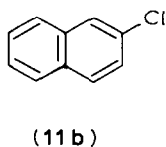
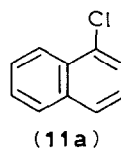
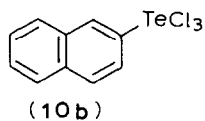
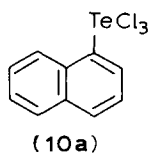
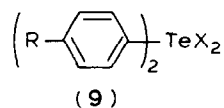
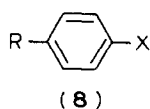
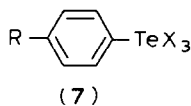
SCHEME 1

isomer ratio of *trans* to *cis* of the dichloride was 93/7, showing that the substitution reaction proceeds mainly with retention of configuration. By similar treatment of the corresponding triiodide **2**, which was prepared from **1** and KI in ethanol [7], *trans*-1-chloro-2-iodocyclohexane (**4**) was obtained (64% yield) as the sole product. No olefinic or alcoholic products were formed in either case. The reaction also proceeded in acetic acid or acetonitrile as the solvent, although the yield was slightly lower. It has been confirmed separately that **1** does not give any **3** under similar conditions without *t*-BuOOH.

A similar reaction occurred with 2-chloro-1-decyltellurium trichloride (**5**; $\text{R} = \text{C}_8\text{H}_{17}$) [6] and 2-chloro-3-phenylpropyltellurium trichloride (**5**; $\text{R} = \text{PhCH}_2$) to give 1,2-dichlorodecane (**6**; $\text{R} = \text{C}_8\text{H}_{17}$) and 1,2-dichloro-3-phenylpropane (**6**; $\text{R} = \text{PhCH}_2$), respectively (40–70% yield). All reactions including those of **1** and **2** did not proceed at room temperature even when left for a longer time (24 h).

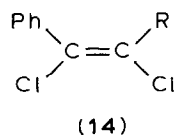
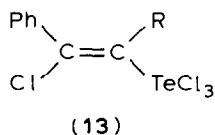


When this reaction was applied to various aryltellurium trihalides (**7** [8] and **10** [9]), the corresponding aryl halides **8** and **11** were formed in 30–50% yield under similar conditions as above. Here, it is worthwhile noting that the substitution occurs completely at the *ipso*-position and thus 1- and 2-substituted naphthalenes (**10a** and **10b**) gave only the corresponding naphthyl chlorides (**11a** and **11b**), respectively. In the cases of these aryl compounds, acetic acid was revealed to be a better solvent than 1,4-dioxane. Diaryltellurium dihalide (**9**) [10], on the other hand, did not produce the corresponding aryl halide **8** under various reaction conditions. Treat-



ment of 4-methoxyphenyl(2-chlorocyclohexyl)tellurium dichloride (**12**) with *t*-BuOOH in acetic acid gave both **3** and **8** (R = MeO, X = Cl) in 55 and 22% yield, respectively. This result is consistent with the above-described observation that the yield of **3** from **1** was higher than that of **8** (R = MeO, X = Cl) from **7** (R = MeO, X = Cl). Namely, the alkyl group is more susceptible to this oxidative α -elimination reaction than the aryl group.

The (*Z*)-alkenyltellurium compounds **13** [3] afforded (*Z*)-dichloroalkene **14** together with a small amount of its (*E*)-isomer (ca. 9/1), revealing that the α -elimination mainly occurs with retention of configuration in this case. The yield of **14** from **13** was lower than that of the case of either aryl- or alkyl-tellurium compounds. This result suggests that the reactivity order of this α -elimination is roughly as follows: alkyl > aryl > alkenyl. The results are summarized in Table 1.



The reaction of **1** was also promoted by other oxidizing agents such as hydrogen peroxide, cumene hydroperoxide, and *meta*-chloroperbenzoic acid, but the yield of **3** was generally lower. Compound **7**, however, did not suffer α -elimination when these oxidizing agents were used. Typical results are also shown in Table 1. During the reaction, white to yellow precipitates were formed which might be composed of inorganic tellurium(IV) oxide and/or oxo halides, since they showed hardly any absorption in the IR spectrum and also hardly any carbon and hydrogen by combustion analysis [11].

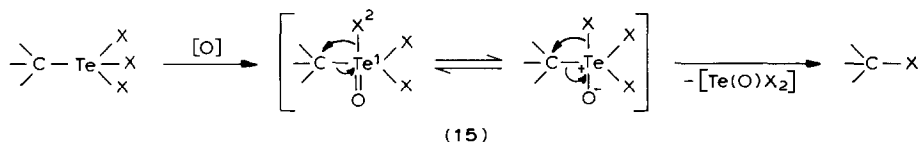
Although the details of the reaction mechanism are not yet clear, several experimental findings should be mentioned to consider a possible reaction scheme. The first possibility is that the reaction involves a radical species such as $R\text{Te}(\text{OR}')\text{X}_3$

TABLE 1
OXIDATIVE α -ELIMINATION OF ORGANIC HALIDES FROM ORGANOTELLURIUM(IV) HALIDES

Te compound (1 mmol)	Oxidant (2 mmol)	Solvent (5 ml)	Reaction time (h)	Reaction temperature (°C)	Product	Yield (%) ^a
1	TBHP ^b	1,4-dioxane	0.5	100	3	92 ^c
1	TBHP	CH ₃ CN	0.5	82	3	51 ^c
1	TBHP	AcOH	2	116	3	84 ^c
2	TBHP	1,4-dioxane	1.5	100	4	64 ^d
1	H ₂ O ₂	1,4-dioxane	1.5	100	3	67 ^c
1	PhC(Me) ₂ OOH	1,4-dioxane	0.7	100	3	44 ^c
1	MCPBA ^e	AcOH	2	116	3	40 ^c
1	t-BuOCl ^f	CH ₃ CN	0.5	82	3	18 ^c
1	t-BuOCl	1,4-dioxane	0.5	100	3	42 ^c
1	(t-BuO) ₂	AcOH	0.5	116	3	17 ^c
5 (R = C ₈ H ₁₇)	TBHP	1,4-dioxane	0.5	100	6 (R = C ₈ H ₁₇)	40
5 (R = PhCH ₂)	TBHP	1,4-dioxane	0.5	100	6 (R = PhCH ₂)	70
7 (R = MeO, X = Cl)	TBHP	1,4-dioxane	2	100	8 (R = MeO, X = Cl)	30
7 (R = MeO, X = Cl)	TBHP	AcOH	1	116	8 (R = MeO, X = Cl)	53
7 (R = Me, X = Cl)	TBHP	AcOH	1.5	116	8 (R = Me, X = Cl)	25
7 (R = MeO, X = Br)	TBHP	AcOH	1.5	116	8 (R = MeO, X = Br)	5
7 (R = Me, X = Cl)	PhC(Me) ₂ OOH	AcOH	1	116	8 (R = Me, X = Cl)	0
10a	TBHP	AcOH	1	116	11a	42
10b	TBHP	AcOH	1	116	11b	60
7 (R = MeO, X = Cl)	t-BuOCl	CH ₃ CN	1	82	8 (R = MeO, X = Cl)	5
7 (R = MeO, X = Cl)	t-BuOCl	1,4-dioxane	1	100	8 (R = MeO, X = Cl)	1
7 (R = MeO, X = Cl)	TBHP + FeSO ₄	AcOH	1	116	8 (R = MeO, X = Cl)	33
7 (R = Me, X = Cl)	TBHP + Fe(lac) ^g	AcOH	1.5	116	8 (R = Me, X = Cl)	5
12	TBHP	AcOH	1	116	3	55 ^c
					8 (R = MeO, X = Cl)	22 ^h
13 (R = H)	TBHP	CH ₃ CN	1	82	14 (R = H)	20 ⁱ
13 (R = Ph)	TBHP	CH ₃ CN	1	82	14 (R = Ph)	30 ⁱ

^a GLC yield. ^b t-BuOOH. ^c *trans/cis* = 93–95/5–7 ^d Only *trans*. ^e *meta*-Chloroperbenzoic acid. ^f t-Butyl hypochlorite. ^g Iron(II) lactate ^h Another product was anisole (6%). ⁱ *Z/E* = 9/1. Smaller amounts (than that of the *E*-isomer) of two or three unidentified products were also formed.

which may be formed by the addition of $R'O\cdot$ to the starting organotellurium(IV) compounds and then it eliminates RX . If the reaction proceeded via such a species, *t*-butoxy or hydroxyl radical should promote the reaction and the product yield might be increased by the addition of Fenton's reagent such as iron(II) sulfate or lactate to the reaction system. The results, however, were the reverse and the yield was rather decreased. Therefore, this possibility may be ruled out. Second, it might be possible that the attacking species is an electrophilic halogen of *t*-butyl hypochlorite ($t\text{-BuOCl}$) which might be formed in situ from *t*-butyl hydroperoxide and the chlorine atom of the starting organotellurium(IV) chlorides by ligand exchange. In fact, we have found that treatment of **1** with commercial $t\text{-BuOCl}$ afforded **3**, although its yield was much lower ($1/2 \sim 1/3$) than that obtained in the reaction of **1** with $t\text{-BuOOH}$ under similar conditions. In the case of **7**, on the other hand, its treatment with $t\text{-BuOCl}$ produced only a trace amount of **8** ($X = \text{Cl}$) (see Table 1). Therefore, this possible scheme also cannot be accepted as the main reaction course. We have recently disclosed the conversion of alkyl phenyl tellurides or telluroxides into the corresponding dialkyl ethers by oxidation with various oxidants in excess in alcohol [12] and proposed organotellurium(VI) species such as tellurone or its analogue as an intermediate where the tellurium moiety becomes a good leaving group. On the other hand, the alcohol formation in the oxidation of some alkyl phenyl tellurides with $t\text{-BuOOH}$ in benzene has been explained by assuming a 1,2-tellurium oxygen shift in either telluroxide or tellurone [13]. By considering these postulations, Scheme 2 seems to be most plausible for this α -elimination at present:

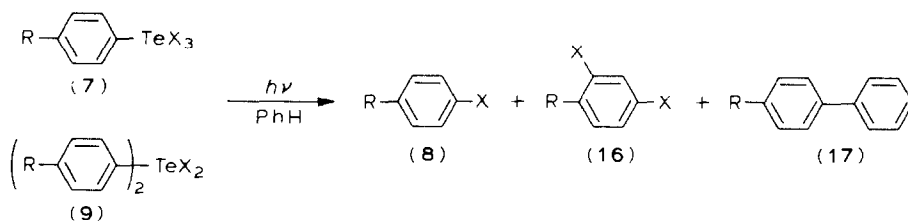


SCHEME 2

organotellurium(IV) halides are oxidized to the corresponding unstable organotellurium(VI) compounds such as **15** in which the tellurium moiety may become a good leaving group and a 1,2-tellurium halogen shift occurs rapidly and intramolecularly to give organic halides. However, the driving force favouring a 1,2-tellurium halogen shift rather than a 1,2-tellurium oxygen shift is not yet known.

Photolytic α -elimination reaction

In a typical reaction, when a benzene (200 ml) solution of 4-methoxyphenyltellurium trichloride (**7**; $R = \text{MeO}$, $X = \text{Cl}$) (1 mmol) was irradiated with a high-pressure mercury lamp at 20–30°C for 1 h in the presence of atmospheric oxygen, *p*-chloroanisole (**8**; $R = \text{MeO}$, $X = \text{Cl}$) was mainly obtained (0.70 mmol, 70% yield) (Scheme 3). Small amounts of 2,4-dichloroanisole (**16**; $R = \text{MeO}$, $X = \text{Cl}$) (2%) and 4-methoxybiphenyl (**17**; $R = \text{MeO}$) (1%) were also formed as by-products, but *o*-chloroanisole was not produced at all. The reaction was accompanied with the deposition of a black tellurium precipitate (0.31 mmol), which may be formed by disproportionation of the performed TeCl_2 [14]. In order to increase the yield of **8** a longer reaction time was required, but the selectivity for **8** decreased. While the



SCHEME 3

photooxidation of benzyltellurium(II) compounds has been known to give oxygen-containing products such as benzaldehyde and benzyl alcohol [15], no oxygen-containing compounds such as *p*-methoxyphenol and quinones were produced in the present photolysis even when the reaction was carried out under an oxygen atmosphere, i.e. *p*-chloroanisole and 2,4-dichloroanisole were obtained in 76 and 2% yield, respectively. It was revealed further that the reaction proceeds even under a nitrogen or argon atmosphere as well, the product yields being almost unaffected. Similar photolysis of 4-methoxyphenyltellurium tribromide (**7**; R = MeO, X = Br) [7] in benzene gave *p*-bromoanisole (**8**; R = MeO, X = Br) in 30% yield. Typical results are shown in Table 2.

In the case of diaryltellurium dichloride (**9**; X = Cl), the product yields were generally lower than those from **7**. Here, the precipitation of tellurium metal was not observed and a mixture of some inorganic tellurium salts and organotellurium compounds was precipitated [16]. The amount of coupling products (**17**) with solvent benzene was increased in these cases (Table 2, Scheme 3). In order to avoid the formation of these coupling products, other organic solvents such as acetic acid, acetonitrile, 1,4-dioxane, and chloroform can be used for this photolysis. In no case, were symmetrical biaryls which might be formed by homo-coupling of the organic moiety of **7** or **9** detected as the products.

The facts that the chlorine and bromine bound to tellurium were introduced selectively into the position where the tellurium moiety was attached previously (*ipso*-substitution) and that solvent benzene was scarcely incorporated represent the characteristic feature of aryltellurium trihalides, since we have confirmed separately that similar photolysis of several arylmetal chlorides (metal = Hg, Tl, or Si) scarcely affords aryl chloride. In the case of arylthallium(III) compounds, only arylated benzenes were obtained in low yields [17].

Taking into account the characteristic feature of the reaction described above that the ligand attached to tellurium can be introduced to the aryl carbon of **7** and **9**, we have tried to make a C-O bond instead of a C-X (X = halogen) bond from aryltellurium(IV) compounds, but the results were not satisfactory. Thus, when bis(4-methoxyphenyl)tellurium diacetate (**9**; R = MeO, X = OAc) [18] was similarly irradiated in acetic acid, *p*-acetoxyanisole (**8**; R = MeO, X = OAc) was formed only in 6% yield. Similar treatment of an acetic acid solution of **7** (R = MeO, X = OAc), prepared in situ from bis(4-methoxyphenyl) ditelluride and lead(IV) acetate [19], produced **8** (R = MeO, X = OAc) in 14% yield. When the reaction was carried out in benzene, a coupling product with benzene was the major product, but its yield was very low.

The reaction proceeded also with alkyl- and alkenyl-tellurium trichlorides such as

1 and **13**, but the yield of the chlorinated product was lower in both cases than that from aryltellurium trichlorides. For example, photolysis of **1** and **13** (R = H) in benzene at 20–25°C for 1 h gave **3** and **14** (R = H) in 28 and 39% yield, respectively. In the latter case, the deposition of black tellurium metal occurred as in the aryl case, while it was hardly observed in the former case. A longer reaction time resulted in the formation of various unidentified compounds at the expense of **3** and **14**. Typical results are also included in Table 2. The highly selective formation of **14** from **13** and that of *trans*-**3** from **1** shows that this photolytic α -elimination occurred mainly with retention of configuration just as the oxidative α -elimination described above.

TABLE 2

PHOTOLYTIC α -ELIMINATION OF ORGANIC HALIDES AND ARYL ACETATES FROM ORGANOTELLURIUM(IV) COMPOUNDS^a

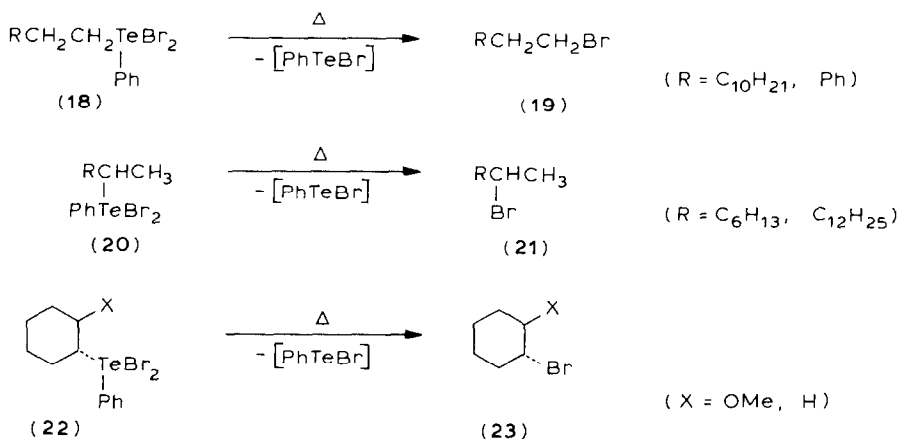
Te compound (1 mmol)	Solvent (200 ml)	Reaction time (h)	Product and yield (%) ^b		
			8	16	17
7 (R = MeO, X = Cl)	benzene	1	70	2	1
7 (R = MeO, X = Cl)	benzene ^c	1	68	2	1
7 (R = MeO, X = Cl)	benzene ^d	1	76	2	trace
7 (R = MeO, X = Cl)	benzene ^e	1	72	2	trace
7 (R = MeO, X = Cl)	benzene	4	81	10	4
7 (R = MeO, X = Cl)	1,4-dioxane ^{f,8}	3	60	0	—
7 (R = MeO, X = Cl)	AcOH ^e	5	40	11	—
7 (R = MeO, X = Cl)	CH ₃ CN	4	41	12	—
7 (R = MeO, X = Cl)	CHCl ₃	4	60	6	—
7 (R = Me, X = Cl)	benzene	4	36	2	trace
7 (R = Me, X = Cl)	AcOH ^f	4	13	3	—
7 (R = H, X = Cl)	benzene	4	7	0	9
7 (R = MeO, X = Br)	benzene	4	30	0	trace
9 (R = MeO, X = Cl)	benzene	4	37	1	6
9 (R = MeO, X = Cl)	benzene ^e	4	23	15	13
9 (R = MeO, X = Cl)	AcOH ^f	4	14	0	—
9 (R = Me, X = Cl)	benzene	4	17	1	13
9 (R = Me, X = Cl)	benzene ^e	4	17	trace	9
9 (R = H, X = Cl)	benzene	4	7	0	9
9 (R = Br, X = Cl)	benzene	4	4	0	12
10a	benzene	4	11a 13	0	0
10b	benzene	4	11b 15	0	0
7 (R = MeO, X = OAc) ^h	benzene	4	1	0	5
7 (R = MeO, X = OAc) ^h	AcOH ^f	4	14	0	—
7 (R = MeO, X = OAc) ^h	Ac ₂ O ^f	4	5	0	—
9 (R = MeO, X = OAc)	benzene	4	1	0	3
9 (R = MeO, X = OAc)	AcOH ^f	4	6	0	—
9 (R = MeO, X = OAc)	CH ₃ CN	4	2	0	—
1	benzene ^f	1	3 28 ⁱ		
1	benzene ^{e,f}	1	3 29 ⁱ		
13 (R = H)	benzene	0.25	14 (R = H)	38 ⁱ	

^a At 20–30°C. ^b GLC yield. ^c Under N₂ atmosphere. ^d Under O₂ atmosphere. ^e (t-BuO)₂ (0.5 mmol) was added. ^f 20 ml. ^g When 200 ml of 1,4-dioxane was used, **8** and anisole were formed in 30 and 50% yield, respectively. ^h Prepared in situ from bis(4-methoxyphenyl) ditelluride and lead(IV) acetate. ⁱ Only *trans*-isomer. ^j *E*-Isomer 1%.

Such three experimental observations as the selective formation of a carbon-halogen bond at the *ipso*-position, the retentive elimination, and the very limited incorporation of solvent benzene show that the photolysis of organotellurium trihalides does not involve a carbon-centred radical in the main reaction course even if radical fission of the C-Te bond and/or the Te-Cl bond occurs. Moreover, we have confirmed that the addition of di-*t*-butyl peroxide to the reaction system of **1**, **7** (R = MeO, X = Cl), and **9** (R = MeO or Me, X = Cl) does not greatly affect the yield and ratio of the product (Table 2). This fact suggests that the reaction cannot be enhanced even if such a radical species as $R\dot{T}eX_3Z$ (Z = OR, halogen, etc.) is involved. Diorganyl tellurides are known to be light and oxygen-sensitive, and it is said that some of them must be treated in a dark room under red light [20], otherwise they are easily oxidized to the corresponding telluroxides or dihydroxytellurium compounds [21]. Although these known facts together with the oxidative α -elimination described above may suggest initial photooxidation of the employed tellurium compounds followed by α -elimination as a possible reaction scheme, this possibility may be ruled out since the reaction also proceeded under a nitrogen or argon atmosphere. For the present, we assume that the photo-induced intramolecular 1,2-tellurium halogen shift operates in organotellurium(IV) halides for this α -elimination.

Pyrolytic α -elimination reaction

When *n*-dodecyl (phenyl)tellurium dibromide (**18**; R = C₁₀H₂₁) [22] was heated at 230–250°C in a Kugelrohr distillation apparatus under reduced pressure (3 Torr) without solvent, *n*-dodecyl bromide (**19**; R = C₁₀H₂₁) was obtained as a distillate in 90% yield. Similarly, thermal decomposition of **18** (R = Ph), **20** (R = C₆H₁₃), and **20** (R = C₁₂H₂₅) [22] afforded the corresponding bromide in over 80% yield (Scheme 4). In all cases, red-brown oily compounds (supposed to contain PhTeBr [23]) were



SCHEME 4

left in the apparatus and were solidified to grey solids by standing at room temperature under an ambient atmosphere. Here, the replacement of the tellurium moiety by halogen occurred selectively at the *ipso*-position just as the photo- and peroxide-induced α -elimination reaction described above. Similar pyrolysis of the

methoxytelluration product of cyclohexene **22** (X = OMe) [24] gave *trans*-1-bromo-2-methoxycyclohexane (**23**; X = OMe) in 70% yield, while that of cyclohexyl(phenyl)tellurium dibromide (**22**; X = H) [22] produced the expected cyclohexyl bromide **23** (X = H) together with an appreciable amount of the unexpected cyclohexene. In no case was bromobenzene detected as a product. Typical results are shown in Table 3. When this reaction was applied to alkyl- and aryl-tellurium trichlorides such as **1** and **7**, no halogen-containing products were produced.

We have already shown the formation of olefins by the pyrolysis of alkyl phenyl telluroxides at 200–240°C [22]. In that case, their formation was accompanied with the formation of the corresponding alcohol, probably via a 1,2-tellurium oxygen shift in the telluroxides. The pyrolytic elimination described here may proceed similarly via a 1,2-tellurium halogen shift, although it is not yet clear whether the reaction involves a radical or an ionic intermediate. It is worthwhile noting that thermal decomposition of tetraphenyltellurium has been suggested to proceed via a radical cage [25] and also that some alkyl(phenyl)tellurium dihalides produce the corresponding alkyl halides by heating them in DMF or ethanol as the solvent [26].

Experimental

¹H NMR spectra were recorded using Varian EM 360 (60 MHz) and JEOL JNM FX-100 (100 MHz) instruments in CDCl₃ with Me₄Si as internal standard. The ¹³C NMR spectrum was taken at 25.1 MHz with a JEOLCO ¹³C Fourier transform NMR system and was recorded in CDCl₃ after 250–1000 pulses with intervals of 2.7–2.8 s. IR spectra were taken with a Hitachi EPI-S2 spectrometer. GLC analyses were carried out using a Shimadzu 4CMPF apparatus using EGSS-X (15%)-Chromosorb-W (1m and 3m), Silicone QF-1(30%)-Chromosorb-W (1 m and 3 m), Apiezon-L(25%)-Shimalite (1 m), and Bentone 34 + DNP(6%)-Shimalite (1 m) columns (N₂ as carrier gas). Commercially available *p*-chloroanisole, *p*-chlorotoluene, chlorobenzene, *p*-bromochlorobenzene, *p*-bromoanisole, α -chloronaphthalene, β -chloronaphthalene, 2,4-dichloroanisole, 2,4-dichlorotoluene, *trans*-1,2-dichlorocyclohexane, *n*-dodecyl bromide, β -phenylethyl bromide, *sec*-tetradecyl bromide, *sec*-octyl bromide, and cyclohexyl bromide were used as authentic samples for GLC analyses. *cis*-1,2-Dichlorocyclohexane [27a], **4** [27b], **14** (R = H) [28], **14** (R = Ph) [28], and **17** (R = MeO, Me, Br) [29] were prepared by the known method. Compound **6** (R = PhCH₂) was prepared by chlorination of allylbenzene with SO₂Cl₂ in

TABLE 3
THERMAL DECOMPOSITION OF ALKYL(PHENYL)TELLURIUM DIBROMIDES

Te compound	mmol	Temperature (°C)/Torr	Product	Isolated yield (%)
18 (R = C ₁₀ H ₂₁)	1	230–250/3	19 (R = C ₁₀ H ₂₁)	90
18 (R = Ph)	1	250/5	19 (R = Ph)	83
20 (R = C ₆ H ₁₃)	1	200–220/30	21 (R = C ₆ H ₁₃)	95
20 (R = C ₁₂ H ₂₅)	1	230–250/2	21 (R = C ₁₂ H ₂₅)	98
22 (X = MeO)	3	200–250/20	23 (X = MeO)	70 ^a
22 (X = H)	2	180–200/3	23 (X = H), 58 and cyclohexene, 39 ^b	

^a Two minor unidentified compounds were also present. ^b Collected in a cold trap at ca. –70 °C.

CCl_4 . Compound **8** ($\text{R} = \text{MeO}$, $\text{X} = \text{OAc}$) was prepared by acetoxylation of commercial hydroquinone monomethyl ether with acetic anhydride in pyridine in the presence of ZnCl_2 . Compound **23** ($\text{X} = \text{OMe}$) was prepared by treatment of cyclohexene with *N*-bromosuccinimide in methanol. All commercial organic and inorganic compounds including *t*-butyl hydroperoxide (70%), *meta*-chloroperbenzoic acid (80%), and hydrogen peroxide (30%) were used without further purification.

Organotellurium(IV) compounds were prepared by the reported method: **1** [5], **2** [7], **5** [6], **7** [8], **9** ($\text{X} = \text{Cl}$) [10], **9** ($\text{R} = \text{MeO}$, $\text{X} = \text{OAc}$) [19], **10** [9], **13** [11], **18** [22], **20** [22], **22** ($\text{X} = \text{H}$) [22], **22** ($\text{X} = \text{OMe}$) [24], diphenyl ditelluride [30], (*p*- MeOC_6H_4)₂ Te_2 [30]. ^1H NMR of **1** (100 MHz) δ 1.35–2.85(m, 8H), 4.72(dt, 1H, *J* 11, 4 Hz), 4.92(dt, 1H, *J* 11, 4 Hz) ppm; ^{13}C NMR δ 24.9(t), 26.5(t), 27.7(t), 37.7(t), 61.7(d), 82.6(d) ppm.

5 ($\text{R} = \text{PhCH}_2$): A mixture of TeCl_4 (10 mmol) and allylbenzene (10 mmol) in CCl_4 (20 ml) was stirred at room temperature for 1 h. Evaporation of the solvent left a deep purple semisolid which was washed with hexane several times to afford a grey powder of **5** ($\text{R} = \text{PhCH}_2$); 70% yield, m.p. (d) 115°C (from CHCl_3 /hexane). IR: 3050, 3000, 2950, 1600, 1500, 1458s, 1440, 1380, 1242, 1220, 1178, 1160, 1082, 1030, 988, 920, 858s, 808, 760s, 708s, 670, 575, 502 cm^{-1} . ^1H NMR (100 MHz): δ 3.04(dd, 1H, *J* = 14, 10 Hz), 3.56(dd, 1H, *J* 14, 5 Hz), 4.18(dd, 1H, *J* 10, 10 Hz), 4.60(dd, 1H, *J* 10, 6 Hz), 5.25(tdd, 1H, *J* 10, 6, 5 Hz), 7.2–7.4(m, 5H) ppm. Found: C, 27.44; H, 2.69. $\text{C}_9\text{H}_{10}\text{Cl}_4\text{Te}$ calcd.: C, 27.89; H, 2.60%.

12: The compound was prepared from 4-methoxyphenyltellurium trichloride (**7**; $\text{R} = \text{OMe}$) and cyclohexene in CHCl_3 by following the reported method for the synthesis of the 2-naphthyl analogue [6]; a white crystalline compound, 90% yield, m.p. 106–107°C (from EtOH). ^1H NMR (100 MHz): δ 1.1–2.8(m, 8H), 3.84(s, 3H), 4.16(ddd, 1H, *J* 11, 11, 6 Hz), 4.64(ddd, 1H, *J* 11, 11, 4 Hz), 7.00(d, 2H), 8.12(d, 2H) ppm. Found: C, 36.80; H, 3.76. $\text{C}_{13}\text{H}_{17}\text{OCl}_3\text{Te}$ calcd.: C, 36.89; H, 4.04%.

UV irradiation of organotellurium compounds was carried out using an Ushio a UM-103B apparatus equipped with a high-pressure mercury lamp. Pyrolysis of organotellurium compounds was carried out using a Kugelrohr distillation apparatus (Büchi GKR-50).

General procedure

Oxidation of 1 with t-butyl hydroperoxide. Compound **1** (0.35 g, 1.0 mmol) was placed in a round-bottomed flask (20 ml) containing 1,4-dioxane (5 ml) with a magnetic stirring bar and a reflux condenser. To the resulting homogeneous solution was added *t*-butyl hydroperoxide (70%, 0.26 g, 2.0 mmol) and the mixture was stirred under reflux for 30 min, during which period a pale yellow solid was precipitated. After the mixture had been cooled to room temperature, the precipitate was removed by filtration, the filtrate was poured into aqueous NaCl and then extracted with diethyl ether (30 ml \times 3), and the ether extract was dried over MgSO_4 . GLC analysis of the extract revealed the presence of **3** (0.14 g, 0.92 mmol, 92%, *cis/trans* 7/93) by using phenyl acetate as an internal standard.

Photolysis of 7 (R = MeO, X = Cl). Compound **7** ($\text{R} = \text{MeO}$, $\text{X} = \text{Cl}$) (0.34 g, 1.0 mmol) was put into a three-necked flask (500 ml), equipped with a reflux condenser and a magnetic stirrer bar, and benzene (200 ml) was added. The resulting homogeneous solution was then irradiated with a high-pressure mercury lamp for 1 h, during which period a black precipitate was deposited. The precipitate was filtered off and

the filtrate was washed with aqueous NaCl and then dried over MgSO₄. GLC analysis of the benzene solution showed the presence of **8** (R = MeO, X = Cl) (0.14 g, 0.7 mmol, 70%), **16** (R = MeO, X = Cl) (0.035 g, 0.02 mmol, 2%), and **17** (R = MeO) (0.018 g, 0.01 mmol, 1%) by using *p*-chlorotoluene, 2,4-dichlorotoluene and 4-methylbiphenyl as internal standards, respectively.

Pyrolysis of 18 (R = C₁₀H₂₁). Compound **18** (R = C₁₀H₂₁) (0.53 g, 1.0 mmol) was heated at 230–250°C without solvent under reduced pressure (3 Torr) using a Kugelrohr distillation apparatus. A colourless liquid was readily obtained as a distillate, which was identical to *n*-dodecyl bromide (**19**; R = C₁₀H₂₁) (0.25 g, 0.90 mmol, 90%) by ¹H NMR and GLC analysis. Red-brown oily compounds (which seemed to consist mainly of PhTeBr (lit. m.p. 70–75°C, red brown powder [23]) were left in the apparatus and were solidified to grey solids on standing at room temperature under ambient atmosphere. The grey solids thus obtained (0.28 g) did not dissolve in either CCl₄ or methanol. They showed strong absorptions of the phenyl group in the IR spectrum: 3050, 1570, 1472s, 1430s, 1325, 1160, 1050, 993s, 910, 835, 730s, 680s, 455, 440 cm⁻¹. Found: C, 26.40; H, 1.92. C₆H₅BrOTe calcd.: C, 23.97; H, 1.68%. The IR spectral data and combustion analytical data suggest that the solids consisted of PhTe(O)Br (major) and the starting dibromide (minor).

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