Telluroxide Elimination by Oxidation of Alkyl Aryl Tellurides: Remarkable Effect of Added Triethylamine

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Treatment of various alkyl phenyl tellurides with 1–2 mol equiv. of *m*-chloroperbenzoic acid in diethyl ether in the presence of triethylamine at 25 °C for 2 h affords the corresponding alkenes highly selectively in fair to good yields. From stereochemical studies using *erythro*- and *threo*-phenyl 3-phenylbutan-2-yl tellurides as substrates it was revealed that, although Et_3N partly facilitates E2 elimination of the telluroxide, the main reaction course is the telluroxide *syn*-elimination (Ei elimination). Without the addition of Et_3N the elimination was quite slow in many cases, and in fact the compounds derived from the addition of *m*-chlorobenzoic acid to tetradecyl and cyclohexyl phenyl telluroxides were isolated, the pyrolysis (~250 °C) of which afforded tetradec-1-ene and cyclohexene, respectively. A 2-pyridyltelluro moiety was revealed for the first time to be a better leaving group than a phenyltelluro moiety in telluroxide elimination.

The selenoxide *syn*-elimination is well known as a double-bond-forming reaction and has been widely used as a useful tool for organic synthesis.[1] On the other hand, studies on the corresponding telluroxide elimination are still very limited and the reaction is not yet generally accepted for such a tool. The examples so far reported are the treatment of secondary alkyl(phenyl)tellurium(IV) dibromides with aq. NaOH[2a] or $NaHCO_3$[2b] and the direct oxidation of secondary alkyl phenyl tellurides with either *tert*-BuOOH[3] or *m*-chloroperbenzoic acid (MCPBA)[4] in organic solvents.† Compared with selenoxide elimination, telluroxide elimination by direct oxidation of tellurides is generally slower, the yield of product alkenes is lower, and side products such as alcohols and ketones are often formed. Since the beneficial effects of various types of added amines upon selenoxide eliminations are well known,[6] we also attempted the telluroxide elimination in the presence of various amines. As a result, we found that the addition of triethylamine to the oxidation system improved the alkene yield and suppressed the formation of the side products. Further, it forced the elimination even from primary alkyl phenyl telluroxides to some extent. It was also found that a 2-pyridyltelluro moiety is a better leaving group than a phenyltelluro moiety and that an elimination occurs smoothly even without addition of the amine. We present here the results of telluroxide elimination by direct oxidation of various alkyl aryl tellurides with several oxidizing agents, mainly with MCPBA, in the presence or absence of various amines, and discuss the reaction pathway by taking account of the stereochemical outcome of the elimination.[4]

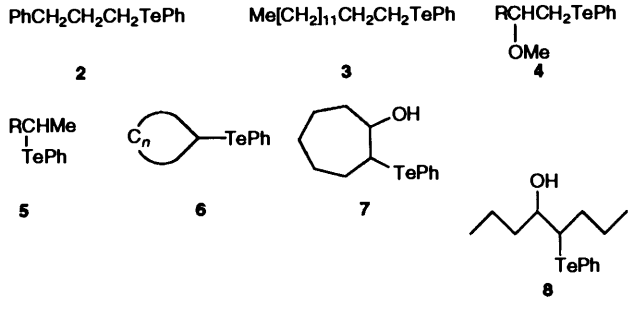
Results and Discussion

Telluroxide Elimination of Phenethyl Phenyl Telluride: Search for the Optimum Reaction Conditions.—First, we examined the most suitable conditions for the elimination using phenethyl phenyl telluride **1** as a substrate. When the telluride was allowed to react with 1 mol equiv. of MCPBA in diethyl ether at 25 °C for 2 h, styrene was obtained in ~ 50% yield together with small amounts of 2-phenylethanol and phenylethanal (Scheme 1). Similar results were obtained when the reactions were conducted for 0.5–3 h. Here we simply thought that benzenetellurenic acid (PhTeOH) formed *in situ* might add to the product styrene or catalyse its polymerization to decrease the yield of styrene, since the starting telluride was not observed after even 0.5 h by TLC monitoring. Therefore, we carried out the same reaction in the presence of a base such as Et_3N, pyridine or 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), hoping to trap the acid. As a result, Et_3N was found to have a remarkable effect in improving both the yield (up to 78%) and selectivity of styrene (Table 1, runs 1, 2, 4 and 5). The elimination also proceeded with other oxidants such as hydrogen peroxide, *tert*-butyl hydroperoxide or sodium periodate in various solvents, typical results being shown in Table 1. Within the attempted experiments the optimum conditions for elimination of telluroxide were revealed to be the use of MCPBA as an oxidant (1–2 mol equiv. compared with the telluride), Et_3N (1 mol equiv.) as a base, and diethyl ether as a solvent at 25 °C for 2 h (Table 1, runs 2 and 6).

$$\underset{\mathbf{1}}{PhCH_2CH_2TePh} \longrightarrow PhCH{=}CH_2 + PhCH_2CH_2OH + PhCH_2CHO$$

Scheme 1 *Reagents:* MCPBA, Et_3N, Et_2O

Elimination of Telluroxide from Various Alkyl Phenyl Tellurides.—Next, various primary alkyl and secondary alkyl phenyl tellurides (**2**–**4** and **5**–**8**, respectively) were treated mainly under the above optimum conditions. For comparison the oxidation was also carried out in the absence of Et_3N. In almost every case, Et_3N showed a striking effect in improving both yield and selectivity of alkenes as had been observed in the



† It is known that the treatment of primary alkyl phenyl tellurides with excess of chloramine-T in refluxing tetrahydrofuran gives terminal alkenes in good yield *via* a telluroxide-elimination-like reaction.[5]

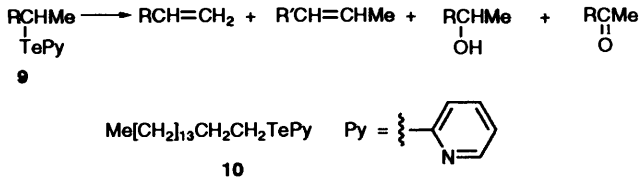
Table 1 Oxidation of phenethyl phenyl telluride **1** under various conditions[a]

Run	Oxidant (mol equiv.)[b]	Base (mol equiv.)[b]	Solvent	Products (GLC yield %)		
				Styrene	2-Phenylethanol	Phenylethanal
1	MCPBA (1)		Et_2O	48	5	2
2	MCPBA (1)	Et_3N (1)	Et_2O	74	0	0
3	MCPBA (1)	Et_3N (2)	Et_2O	36	0	0
4	MCPBA (1)	Pyridine (1)	Et_2O	59	1	9
5	MCPBA (1)	DBU (1)	Et_2O	24	1	0
6	MCPBA (2)	Et_3N (1)	Et_2O	78	5	2
7	MCPBA (4)	Et_3N (1)	Et_2O	3	0	0
8	MCPBA (1)	Et_3N (1)	EtOAc	42	0	0
9	Bu^{t}OOH (1)	Pyridine (1)	Et_2O	44	2	5
10	H_2O_2 (1)	Et_3N (1)	THF	58	0	0
11	$NaIO_4$ (1)	Et_3N (1)	THF	27	0	0

[a] **1** (1 mmol), solvent (5 cm^3), at 25 °C for 2 h. [b] Equivalent to substrate **1**.

oxidation of trial compound **1**. Typical results are shown in Table 2. Telluroxide elimination from primary alkyl phenyl tellurides was generally slow and, in fact, a new organotellurium compound, which was supposed to be the telluride–MCPBA adduct or the telluroxide–*m*-chlorobenzoic acid (MCBA) adduct, was isolated from compound **3** as will be described later. None of elimination products, methyl vinyl ethers, were produced by oxidation of compounds **4** (R = Ph, $[CH_2]_7Me$) even in the presence of Et_3N, although the starting material **4** was not observed by TLC after the oxidation. The structure of the oxidized species, however, could not be determined. In the case of acyclic secondary alkyl tellurides **5**, the reactivity for elimination depended much on the alkyl group's chain length when the oxidation was carried out in the absence of Et_3N. For example, elimination was quite slow for substrates **5** (R = $[CH_2]_5Me$) and **5** (R = $[CH_2]_7Me$) and afforded the corresponding alkenes in only 9–16% yield after reaction for 2 h,* while alkenes were produced in 54% yield from **5** (R = $[CH_2]_{11}Me$). By the addition of Et_3N to the reaction system, however, the reaction was much accelerated and the yield of alkene increased from 9–16 to 68–70% in the former cases and from 54 to 85% in the latter case, respectively. In the case of cycloalkyl phenyl tellurides **6** except for cyclohexyl case (**6**; n = 3) elimination was rather fast even in the absence of Et_3N, but the effect of added amine appeared in the highly selective formation of alkenes as has been observed for substrates **1**, **3** and **5**. In contrast, from compound **6** (n = 3) a stable adduct between the corresponding telluroxide and MCBA was produced as in the case of **3** (*vide post*). In the case of the 2-hydroxyalkyl phenyl tellurides **7** and **8** the product is only the allylic alcohol and its yield increased upon addition of Et_3N to the initial mixture. All results are summarized in Table 2.

It is known that a pyridylseleno moiety is a better leaving group than a phenylseleno moiety in selenoxide elimination because of its electron-withdrawing properties.[7] Since there are no reports on telluroxide elimination using an aryltellurium moiety other than a PhTe moiety, we attempted the oxidation of



Scheme 2 *Reagents:* H_2O_2, THF

several alkyl 2-pyridyl tellurides (**9** and **10**) and compared the results with those obtained with the corresponding phenyl tellurides (Scheme 2). Under the oxidation conditions so far described the yield of alkenes from substrates **9** was insufficient, but it was much improved by using H_2O_2 as an oxidant. Importantly, in this case Et_3N was not necessary and yet the yield of alkene was much higher than for the corresponding phenyl tellurides {compare the results from **5** (R = $[CH_2]_7Me$, $[CH_2]_{11}Me$) with those from the corresponding pyridyl analogue **9**, and also those of compounds **3** and **10**}. Here, the 2-pyridinetellurenic acid (2-PyTeOH) formed *in situ* may be a neutral species in the form of 2-PyH$^+$ TeO$^-$. Typical results are shown in Table 2.

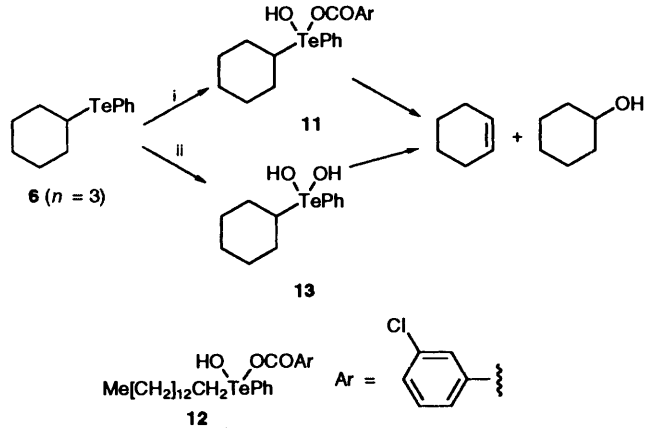
Isolation of the Intermediate Organotellurium Compounds.— It is known that cyclohexyl[2a] and some primary alkyl phenyl telluroxides[2a,8] are sufficiently thermally stable to be isolated. In these cases vigorous conditions such as pyrolysis at 200–240 °C or treatment in refluxing toluene for a long time are required to effect the elimination. In agreement with these observations we found that the oxidation of cyclohexyl and tetradecyl phenyl tellurides [**6** (n = 3) and **3**, respectively] with MCPBA at 25 °C in diethyl ether did not afford any of the corresponding alkenes, alcohols, or ketones, and instead some organotellurium compounds were isolated, as a solid (m.p. 80–82 °C) and as a yellow oil, respectively, in moderate yields. The structure of the solid, and that of the oil, were tentatively assigned as **11** and **12**, respectively, from various spectral data (IR and ^{1}H and ^{13}C NMR) as well as from combustion analytical data (Scheme 3). Namely, the compounds can be considered as the corresponding addition compound between MCBA and the particular telluroxide. The characteristically strong IR absorptions appeared at roughly 2930, 2850, 1600, 1500 and 1330 cm^{-1}. Although a parent peak (M$^+$) for compound **11** was not observed in a high-resolution mass spectral (EI) determination, a fragment peak (M$^+$ − OH) was clearly observed together with several peaks assignable to Ph_2Te^+, $PhTeC_6H_{11}^+$, $Ph_2Te(OCOC_6H_4Cl)^+$, and $PhTe(OCOC_6H_4Cl)_2^+$. When the cyclohexyl telluride **6** (n = 3) was treated with 30% H_2O_2 at 25 °C in tetrahydrofuran (THF), a yellow oil was

* Although some of us reported in ref. 4 that MCPBA oxidation of **5** (R = $[CH_2]_5Me$ and $[CH_2]_7Me$) for 2 h produced the corresponding alkenes in 52 and 48% yield, respectively, this is incorrect. It was found that in these reactions, after the oxidation, treatment with N_2H_4 is indispensable in reducing the produced telluroxides to the tellurides, otherwise the telluroxides were thermally decomposed to give alkenes at an injection port in GLC determination, making analysis inaccurate. We would like to append our correction as shown in Table 2. Although in the case of compounds **1** and **5** (R = $[CH_2]_{11}Me$) the yield of alkenes did not change much with or without treatment with N_2H_4, the yields of the products in this report were all determined after treatment with N_2H_4.

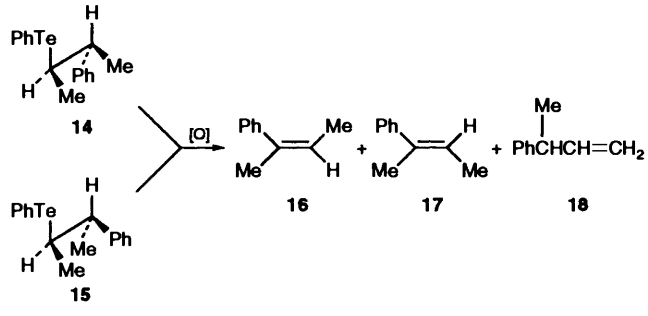
Table 2 Oxidation of various alkyl aryl tellurides with MCPBA[a]

Telluride[b]	MCPBA[c] (mol equiv.)	Base[c] (1 mol equiv.)	Solvent (5 cm^3)	Products (GLC yield %)
1	1	Et_3N	Et_2O	styrene (74)
1	1		Et_2O	styrene (48), 2-phenylethanol (5), phenylethanal (2)
2	2	Et_3N	Et_2O	allylbenzene (40)
2	2		Et_2O	allylbenzene (trace)
3	2	Et_3N	Et_2O	tetradec-1-ene (25)
3	2	Et_3N	Et_2O[d]	tetradec-1-ene (34), tetradecan-1-ol (8)
3	2		Et_2O	tetradec-1-ene (0)[e]
3	2	Et_3N	EtOAc[f]	tetradec-1-ene (51), tetradecan-1-ol (5)
4 (R = Ph)	2	Et_3N	Et_2O	1-methoxystyrene (0)[g]
4 (R = $[CH_2]_7Me$)	2	Et_3N	Et_2O	2-methoxydec-2-ene (0)[g]
5 (R = $[CH_2]_5Me$)	2	Et_3N	Et_2O	oct-1-ene (34), (*E*)-oct-2-ene (20), (*Z*)-oct-2-ene (14)
5 (R = $[CH_2]_5Me$)	1		Et_2O	oct-1-ene (2), (*E*)-oct-2-ene (4), (*Z*)-oct-2-ene (3), octan-2-ol (10), octan-2-one (trace)
5 (R = $[CH_2]_7Me$)	2	Et_3N	Et_2O	dec-1-ene (40), dec-2-enes (30), decan-2-ol (2), decan-2-one (4)
5 (R = $[CH_2]_7Me$)	1		Et_2O	dec-1-ene (4), dec-2-enes (12), decan-2-ol (7), decan-2-one (3)
5 (R = $[CH_2]_{11}Me$)	2	Et_3N	Et_2O	tetradec-1- and -2-enes (85),[h] tetradecan-2-ol (3), tetradecan-2-one (3)
5 (R = $[CH_2]_{11}Me$)	1.5		Et_2O	tetradec-1- and -2-enes (54),[i] tetradecan-2-ol (1), tetradecan-2-one (2)
6 (*n* = 4)	2	Et_3N	Et_2O	cycloheptene (66)
6 (*n* = 4)	1		Et_2O	cycloheptene (70), cycloheptanol (1), cycloheptanone (8)
6 (*n* = 5)	2	Et_3N	Et_2O	cyclooctene (58)
6 (*n* = 5)	1		Et_2O	cyclooctene (69), cyclooctanol (7), cyclooctanone (19)
6 (*n* = 9)	2	Et_3N	Et_2O	(*E*)-cyclododecene (76), (*Z*)-cyclododecene (18)
6 (*n* = 9)	1		Et_2O	(*E*)-cyclododecene (67), cyclododecanol (7), cyclododecanone (7)
7	2	Et_3N	Et_2O	cyclohept-2-enol (57)[j]
7	1		Et_2O	cyclohept-2-enol (46)[j,k]
8	2	Et_3N	Et_2O	oct-5-en-4-ol (64)[j]
8	1		Et_2O	oct-5-en-4-ol (42)[j,k]
9 (R = $[CH_2]_7Me$)	2[l]		THF	dec-1- and -2-enes (47), decan-2-ol (19), decan-2-one (8)
9 (R = $[CH_2]_{11}Me$)	2[l]		THF	tetradec-1- and -2-enes (71),[m] tetradecan-2-ol (6), tetradecan-2-one (11)
10	2[l]		THF	hexadec-1-ene (33)

[a] At 25 °C for 2 h except where otherwise mentioned. [b] 0.5–1 mmol. [c] Equivalent to the telluride. [d] For 1 week. [e] Compound **12**, the adduct between the telluroxide of **3** and MCBA, was obtained in 67% yield. See the text and the Experimental section. [f] At reflux. [g] All starting telluride was consumed, but the product was not identified (see the text). [h] 1-:2- 60:40. [i] 1-:2- 63:37. [j] Isolated yield. [k] Several unidentified compounds were also produced. [l] H_2O_2 (30%) was employed as an oxidant. [m] 1-:2- 54:46.



Scheme 3 *Reagents:* i, MCPBA (1 mol equiv.), Et_2O; ii, H_2O_2 (1 mol equiv.), THF



Scheme 4

obtained, the IR spectrum of which was quite similar to that of the reported cyclohexyl phenyl telluroxide hydrate (a white solid)[2a] obtained by treatment of the corresponding dibromide with aq. NaOH. Although its structure is not clear, we tentatively assign it as **13**. Pyrolysis of compounds **11** and **13** at 220–250 °C at 760 mmHg in a Kugelrohr apparatus gave cyclohexene and cyclohexanol in 15 and 3% and 51 and 11% isolated yield, respectively. Similar pyrolysis of compound **12** gave tetradec-1-ene (50%), tetradecan-1-ol (10%) and tetradecanal (8%). On the other hand, treatment of compounds **11** and **12** with Et_3N (1 mol equiv.) in diethyl ether at 25 °C for 2 h afforded cyclohexene (9% by GLC) and tetradec-1-ene (20% by GLC), respectively. These results suggest that Et_3N effects the elimination of MCBA from the adduct to give the telluroxide which eliminates alkenes much more easily.

Stereochemistry of Telluroxide Elimination in the Presence or Absence of Et_3N.—Elimination of telluroxide has been reported to proceed *via syn*-elimination (Ei) in Bu^tOOH oxidation of *threo*-phenyl-3-phenylbutan-2-yl telluride **14** and its *erythro*-isomer **15** (detailed conditions not specified) as in the case of selenoxide elimination[3] (Scheme 4). In previous sections we have shown the occurrence of a remarkable effect of added Et_3N, namely an improvement in both yield and selectivity of

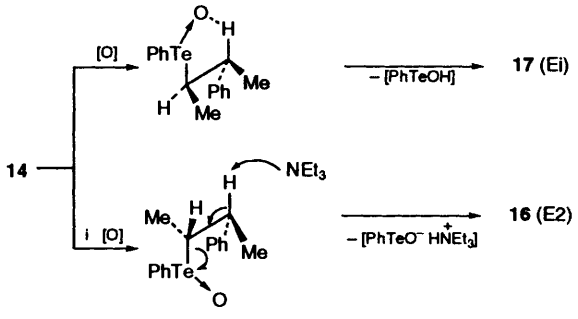
Table 3 Oxidation of stereoisomeric tellurides **14** and **15** with MCPBA

Run	Telluride (0.5 mmol)	MCPBA (mol equiv.)[a]	Base (1 mol equiv.)[a]	Solvent (5 cm^3)	Temp. (T/°C)	Time (t/h)	Products (GLC yield %) 16	17	18	Total yield (%)
1	**14**	2	Et_3N	Et_2O	25	2	2	6	16	24
2	**14**	1		Et_2O	25	2	0	6	19	25
3	**14**	2	Et_3N	EtOAc	77[b]	3	9	12	21	42
4	**14**	1		EtOAc	77[b]	3	0	11	16	27
5[c]	**14**	Bu'OOH		Benzene			0	9	26	35
6	**15**	2	Et_3N	EtOAc	77[b]	3	17	8	45	70
7	**15**	1		EtOAc	77[b]	3	16	0	46	62
8[c]	**15**	Bu'OOH		Benzene			5	0	27	32

[a] Equivalent to the telluride. [b] At reflux. [c] Data from ref. 3. Detailed conditions were not reported.

alkenes. The amine may play a role in trapping the produced acids such as PhTeOH and MCBA and/or facilitating formation of the telluroxide rather than the adduct, but there might also be some other reasons for such an improvement. In order to know whether Et_3N affects the stereochemical course of the reaction, we chose diastereoisomers **14** and **15** as substrates and carried out the elimination under several different conditions. Three alkenes (**16**, **17** and **18**) were the products. Typical results are summarized in Table 3.

In MCPBA oxidation in the absence of Et_3N, only *E*-alkene **17** was obtained stereospecifically from *threo*-telluride **14** as an internal alkene, and only *Z*-alkene **16** from *erythro*-isomer **15**, irrespective of the kind of solvent and reaction temperature (Table 3; runs 2, 4 and 7). The results clearly show the occurrence of *syn*-elimination (Ei), supporting the reported similar observation in the Bu'OOH oxidation in benzene.[3] On the other hand, in the oxidation in the presence of Et_3N, elimination is not stereospecific and the formation of a certain amount of an isomeric alkene, **16** from **14** and **17** from **15**, was also observed. Since we have confirmed separately that no isomerization occurs within alkenes **16**–**18** (by GLC) and also that no epimerization occurs between diastereoisomers **14** and **15** (by ^1H NMR spectroscopy) under the present conditions, the above results suggest that E2 elimination pathways as shown in Scheme 5 occurred concomitantly. There might be a rapid



Scheme 5 *Conditions:* i, oxidation carried out in presence of Et_3N

epimerization at the proton site adjacent to the Te–O bond by the effect of Et_3N, but in that case we should expect the formation of isomers **16** and **17** in the same isomer ratio in runs 3 and 6 in Table 3.

Reason for a Remarkable Effect of Et_3N.—Taking account of these stereochemical observations, the reason for the increase in both yield and selectivity of alkenes by addition of Et_3N can be summarized as follows. (1) The amine may react with the produced acid MCBA and generally prevent the formation of the MCBA–telluroxide adducts such as **11** and **12**. Alternatively, it may effect the elimination of MCBA from the first formed adducts to give the telluroxides. The carbonyl oxygen of telluroxides has a stronger basicity than the oxygen of such adducts, leading to ready elimination of telluroxide. (2) It causes E2 elimination as well as an increase in yield of the alkene. (3) It may react with PhTeOH formed *in situ* by telluroxide elimination and prevent its addition to the produced alkenes to form some tellurenic ester (ROTePh). Side products such as alcohols, ketones and aldehydes might be produced through such an ester.

Experimental

^1H and ^{13}C NMR spectra were recorded on JEOL GSX-270 (270 MHz) and JNM FX-100 (100 MHz) spectrometers for solutions in $CDCl_3$. Chemical shifts are reported in δ-units downfield from the internal reference Me_4Si, and J-values are given in Hz. IR spectra were recorded on Perkin-Elmer 521 and JASCO IR-810 infrared spectrophotometers for KBr pellets and paraffin mulls (for solids) or thin films (for liquids). M.p.s were determined on a Yanaco MP-S3 micro melting point apparatus and are uncorrected. GLC analyses were performed on a Hitachi 163 instrument (1 m × 3 mm stainless steel column packed with 20% PEG on Shimalite) and a Shimadzu GC-14A instrument (25 m HiCap-CBP-10-S25 capillary column) with flame-ionization detectors and N_2 as carrier gas. Column chromatography on SiO_2 was performed with Wakogel C-300 [hexane and hexane–ethyl acetate (9:1) as eluent]. Elemental analyses were performed at the Microanalytical Center of Kyoto University.

All oxidation products such as alkenes, alcohols, and ketones except for phenylbutenes are commercially available compounds which were used as authentic samples for GLC analysis. 3-Phenylbut-1-ene was prepared by Wittig reaction[9] of methylidenetriphenylphosphine with 2-phenylpropanal in 69% isolated yield: δ[10] 1.36 (3 H, d, J 7.0), 3.45 (1 H, m), 5.01 (1 H, m), 5.06 (1 H, m), 6.00 (1 H, m) and 7.16–7.33 (5 H, m). Similarly, a ~3:2 isomeric mixture (GLC, ^1H NMR) of 2-phenylbut-2-enes was prepared by Wittig reaction[9] of ethylidenetriphenylphosphine with acetophenone in 45% isolated yield. By comparison of the NMR spectral data with those reported[10] we could assign the major and minor component as the *E*- and *Z*-isomer, respectively: δ (*E*-isomer) 1.79 (3 H, dq, J 6.97 and 1.10), 2.02 (3 H, m), 5.36 (1 H, qq, J 6.97 and 1.47) and 7.17–7.38 (5 H, m); (*Z*-isomer) 1.59 (3 H, dq, J 6.96 and 1.83), 2.01 (3 H, m), 5.56 (1 H, qq, J 6.78 and 1.83) and 7.17–7.38 (5 H, m). The retention time of each compound in GLC (25 m capillary column) was in the following increasing order; 3-phenylbut-1-ene < (*Z*)-2-phenylbut-2-ene < (*E*)-2-phenylbut-2-ene.

The following organic ditellurides and tellurides were prepared by reported methods: diphenyl ditelluride,[11] di-2-pyridyl ditelluride,[12] phenethyl phenyl telluride **1**,[2a] phenyl tetradecyl telluride **3**,[2a] 2-methoxy-2-phenylethyl phenyl telluride (**4**; R = Ph),[2a] 2-methoxydecyl phenyl telluride (**4**; R = $[CH_2]_7Me$),[2a]

octan-2-yl phenyl telluride (**5**; R = $[CH_2]_5Me$),[2a] decan-2-yl phenyl telluride (**5**; R = $[CH_2]_7Me$),[2a] phenyl tetradecan-2-yl telluride (**5**; R = $[CH_2]_{11}Me$),[2a] cyclohexyl phenyl telluride (**6**; n = 3),[2a] cycloheptyl phenyl telluride (**6**; n = 4),[2a] cyclooctyl phenyl telluride (**6**; n = 5),[2a] cyclododecyl phenyl telluride (**6**; n = 9),[2a] 2-hydroxylcycloheptyl phenyl telluride **7**,[2a] and 5-hydroxyoctan-4-yl phenyl telluride **8**.[2a]

Preparation of New Alkyl Aryl Tellurides.—*Phenyl 3-phenylpropyl telluride* **2**. Prepared from the reaction of 3-phenylpropyl bromide (4 mmol) with $(PhTe)_2$ (2 mmol) and $NaBH_4$ (4 mmol) in EtOH (20 cm^3) at 20–25 °C for 3 h. A *red oil*, 83% isolated yield after column chromatography on SiO_2 with hexane–ethyl acetate (9:1) as eluent: δ 2.07 (2 H, quint., J 7.5), 2.65 (2 H, t, J 7.5), 2.84 (2 H, t, J 7.5), 7.08–7.26 (8 H, m) and 7.66 (2 H, d, J 6.2); δ_C 7.8 (t, PhTe*C*), 33.2 (t), 37.7 (t), 111.6 [s, PhTe, C(1)], 125.8 (d), 127.4 (d), 128.2 (d), 128.4 (d), 129.0 (d), 138.2 (d) and 141.0 [s, Ph, C(1)] (Found: C, 55.8; H, 4.9. $C_{15}H_{16}Te$ requires C, 55.63; H, 4.98%).

threo-*Phenyl 3-phenylbutan-2-yl telluride* **14**. In a two-necked 50 cm^3 round-bottom flask containing a magnetic stirring bar were placed $(PhTe)_2$ (2.0 g, 4.89 mmol) and $NaBH_4$ (0.75 g, 19.9 mmol) under nitrogen. Ethanol (20 cm^3) was added to the flask at 0 °C, and the mixture became homogeneous after being stirred for 0.5 h at room temperature, during which the colour of the solution turned from orange to pale yellow. An ethanolic (30 cm^3) solution of the tosyl derivative of *erythro*-3-phenylbutan-2-ol (2.5 g, 8.22 mmol), prepared by Cram's method,[13] was then added to the resulting solution, and the mixture was stirred at reflux for 4 h. After it had been cooled, the mixture was treated with brine and then extracted with CH_2Cl_2 (3 × 50 cm^3), and the extract was dried over $MgSO_4$. Removal of the solvent under reduced pressure left a red oily residue, which was subjected to column chromatography on SiO_2 [hexane; then hexane–ethyl acetate (9:1)] to give threo-**14** as a *brown orange oil* (0.74 g, 26.7%); δ 1.42 (3 H, d, J 7.0), 1.50 (3 H, d, J 7.3), 2.91 (1 H, m), 3.65 (1 H, m), 7.14–7.31 (8 H, m) and 7.72 (2 H, d, J 7.9); δ_C 21.9 (q), 23.6 (q), 33.2 (d, PhTe-*C*), 47.3 (d), 111.8 [s, PhTe, C(1)], 126.4 (d), 127.3 (d), 127.8 (d), 128.3 (d), 128.9 (d), 140.3 (d) and 145.0 (s) (Found: C, 56.6; H, 5.3. $C_{16}H_{18}Te$ requires C, 56.87; H, 5.37%).

erythro-*Phenyl 3-phenylbutan-2-yl telluride* **15**. The *telluride* was similarly prepared as above from the corresponding *threo*-tosylate (3.56 g, 11.7 mmol) as a red oil (0.88 g, 22.3%); δ 1.40 (3 H, d, J 7.0), 1.56 (3 H, d, J 7.0), 3.00 (1 H, quint., J 7.0), 3.75 (1 H, quint., J 7.0), 7.12–7.29 (8 H, m) and 7.75 (2 H, d, J 8.2); δ_C 18.8 (q), 21.1 (q), 33.2 (d, PhTe*C*), 46.6 (d), 112.8 [s, PhTe, C(1)], 126.6 (d), 127.4 (d), 127.8 (d), 128.3 (d), 129.0 (d), 140.2 (d) and 145.2 (s) (Found: C, 56.6; H, 5.3%).

Alkyl 2-pyridyl tellurides **9** and **10** were similarly prepared by reaction of the corresponding alkyl bromides or toluene-*p*-sulfonates (4 mmol) with di-2-pyridyl ditelluride (2 mmol) and $NaBH_4$ (4–5 mmol) in dry ethanol (20–30 cm^3) under N_2 at reflux for 8 h, and were isolated by column chromatography on SiO_2 with hexane–ethyl acetate (9:1) as eluent. The tellurides are slightly unstable in air and should be kept under N_2 for storage. A slight decomposition to give black tellurium was observed during chromatography and sometimes it was difficult to obtain a pure sample for combustion analysis. Attempts at the preparation of phenethyl and 3-phenylpropyl 2-pyridyl tellurides were unsuccessful by this method and resulted in the formation of diphenethyl and bis-3-phenylpropyl ditellurides, respectively.

Decan-2-yl 2'-pyridyl telluride (**9**; R = $[CH_2]_7Me$). A *yellow oil*, 26% isolated yield; δ 0.88–1.89 (20 H, m), 3.87 (1 H, m), 7.05 (1 H, m), 7.34 (1 H, m), 7.55 (1 H, m) and 8.50 (1 H, m); δ_C 14.1 (q), 22.6 (t), 24.7 (q), 26.2 (d, PhTe*C*), 29.2 (t), 29.3 (t), 29.4 (t), 29.5 (t), 31.8 (t), 39.7 (t), 121.1 (d), 133.1 (d), 135.3 (d), 142.0 [s, PyTe, C(2')] and 150.8 (d) (Found: C, 51.6; H, 7.0; N, 3.75. $C_{15}H_{25}NTe$ requires C, 51.93; H, 7.26; N, 4.04%).

2'-Pyridyl tetradecan-2-yl telluride (**9**; R = $[CH_2]_{11}Me$). A *yellow oil*, 40% isolated yield; δ 0.86–1.89 (25 H, m), 1.79 (3 H, d), 3.85 (1 H, m), 7.04 (1 H, m), 7.34 (1 H, m), 7.55 (1 H, m) and 8.50 (1 H, m); δ_C 15.1 (q), 23.7 (t), 25.5 (q), 27.2 (d, PhTe*C*), 30.2 (t), 30.3 (t), 30.3 (t), 30.4 (t), 30.5 (t), 30.6 (t), 30.7 (t), 32.9 (t), 40.4 (t), 40.7 (t), 122.1 (d), 134.0 (d), 136.3 (d), 143.0 [s, PyTe, C(2')] and 151.8 (d) (Found: C, 56.3; H, 8.3; N, 3.2. $C_{19}H_{33}NTe$ requires C, 56.62; H, 8.25; N, 3.47%).

Hexadecyl 2'-pyridyl telluride **10**. A *yellow oil*, 36% isolated yield; δ 0.85–1.93 (31 H, m), 3.12 (2, H, m), 7.01 (1 H, m), 7.31 (1 H, m), 7.47 (1 H, m) and 8.47 (1 H, m); δ_C 10.7 (t, PhTe*C*), 15.1 (q), 23.7 (t), 27.2 (t), 29.9 (t), 30.0 (t), 30.2 (t), 30.4 (t), 30.5 (t), 30.6 (t), 30.7 (t), 30.8 (t), 32.3 (t), 32.8 (t), 32.9(t), 33.2 (t), 121.9 (d), 132.7 (d), 136.3 (d), 142.2 [s, PyTe, C(2')] and 151.8 (d) (Found: C, 58.3; H, 8.7; N, 3.25. $C_{21}H_{37}NTe$ requires C, 58.50; H, 8.65; N, 3.25%).

General Procedure for Telluroxide Elimination by Oxidation of Alkyl Phenyl Tellurides in the Presence of Base.—To a two-necked round-bottom flask (25 cm^3) containing alkyl phenyl telluride (1 mmol), triethylamine (1–2 mmol) and diethyl ether (5 cm^3) was added solid MCPBA (purity 80%) (2 mmol as pure MCPBA) portionwise at 25 °C and the mixture was stirred with a magnetic stirrer for 2 h at the same temperature before being poured into saturated aq. Na_2CO_3 (100 cm^3) containing hydrazine (10 cm^3) and the mixture was stirred for 0.5 h to remove the resulting MCBA and also to reduce the remaining MCPBA and telluroxide to MCBA and telluride, respectively. The solution was extracted with diethyl ether (3 × 50 cm^3) and the extract was dried over $MgSO_4$ and analysed by GLC using a suitable internal standard. In the case of 2-hydroxyalkyl phenyl tellurides, the product was isolated by column chromatography on SiO_2 [hexane–ethyl acetate (9:1)].

Isolation of Cyclohexyl Phenyl Telluride–MCPBA Adduct **11**.—A mixture of cyclohexyl phenyl telluride (**6**; n = 3) (0.335 g, 1.16 mmol) and 80% MCPBA (0.253 g, 1.17 mmol as pure MCPBA) in diethyl ether (15 cm^3) was stirred at 25 °C for 2 h in a two-necked 20 cm^3 round-bottom flask with a magnetic stirrer. The resulting precipitate was collected on a glass filter and dried *in vacuo* (0.280 g, 52% yield as the adduct **11**); m.p. 80–82 °C. The solid is soluble in aq. 0.5 mol dm^{-3} NaOH, but insoluble in aq. Na_2CO_3; δ 0.8–2.6 (11 H, m), 3.1–3.8 (1 H, m), 6.9–7.7 (5 H, m), 7.7–8.1 (4 H, m); δ_C 25.7 (t), 28.2 (t), 29.5 (t), 60.6 (d, cyclohexyl *C*-Te), 127.7 (d), 129.2 (d), 129.5 (d), 129.7 (d), 130.0 (s), 131.0 (s), 131.2 (d), 133.0 (d), 134.0 (s, phenyl *C*-Te), 136.4 (s) and 171.2 (s); ν_{max}(KBr disk)/cm^{-1} 3600–3300br, 3050, 2940s, 2850, 1605s, 1560s, 1475, 1450, 1420, 1335vs, 1260, 1180, 1065, 990, 865, 760s, 735s, 680, 610s, 540, 490, 455 and 400; ν_{max}(paraffin mull)/cm^{-1} 3050, 2920br, 2850, 1605s, 1560s, 1460, 1420, 1375, 1335vs, 1260, 1175, 1150, 1065, 985, 860, 775s, 735s, 680, 610s, 540, 450 and 400; HRMS (exact mass) [Found: m/z, 445.0201. $C_{19}H_{20}ClO_2Te$ (M − OH) requires m/z 445.0214] (Found: C, 49.0; H, 4.7. $C_{19}H_{21}ClO_3Te$ requires C, 49.57; H, 4.60%).

Isolation of phenyl tetradecyl telluride–MCPBA adduct **12**. A *yellow oil* (67%); δ 0.80–1.40 (27 H, m), 3.03 (2 H, br), 7.2–7.4 (5 H, m) and 7.8–7.9 (4 H, m); δ_C 14.1 (q), 22.7 (t), 24.9 (t, PhTe*C*), 29.2 (t), 29.3 (t), 29.4 (t), 29.4 (t), 29.5 (t), 29.6 (t), 29.7 (t), 29.7 (t), 31.4 (t), 31.6 (t), 32.0 (t), 127.6 (d), 129.1 (d), 129.4 (d), 129.6 (d), 130.8 (d), 132.1 (d), 132.4 (s, phenyl *C*-Te), 132.9 (d) and 133.9 (d); ν_{max}(neat)/cm^{-1} 3050, 2900, 2840, 1600s, 1545s, 1455s, 1325vs, 1250s, 1170s, 1140s, 1130s, 1060s, 1010s, 980s, 900s, 860s, 750s, 730s and 690s (Found: C, 56.7; H, 7.2. $C_{27}H_{39}ClO_3Te$ requires C, 56.43; H, 6.84%).

Isolation of cyclohexyl phenyl telluride–H_2O_2 adduct **13**. A

yellow oil (48%); δ 0.80–2.10 (12 H, m), 3.3–3.4 (1 H, m), 7.1–7.3 (3 H, m) and 7.7–7.8 (2 H, m); δ_C 25.8 (t), 27.9 (d, cyclohexyl *C*-Te), 28.1 (t), 36.3 (t), 111.5 (s, phenyl *C*-Te), 127.6 (d), 128.9 (d) and 140.0 (d); ν_{max}(KBr disk)/cm $^{-1}$ 3600–3100br, 3050s, 2930s, 2850s, 1570s, 1480s, 1450s, 1440s, 1340s, 1260s, 1180s, 1060s, 1020s, 1000s, 740s, 700s, 680–500br, 460s and 420s (Found: C, 44.9; H, 5.4. $C_{12}H_{18}O_2Te$ requires C, 44.78; H, 5.64%).

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