employed, and each solution was studied at 5 to 9 pressures ranging from 0 to 180 MPa. For the solvolysis reaction of **1**, 0.01 M solutions of KOH were used instead of the buffers; it was verified that the slight differences in ionic strength between these solutions had no effect.

Calculations. All observed rate constants are based on the first two half-lives, with 15-20 points of regular time intervals being read directly from the recording. The first-order expressions fit in all cases with correlation constants of at least 0.999. The constants found are converted to those for a pH of 10 for **1** and of 8 for **2**. The data for **1** at each pressure are then used to construct Eadie plots based on $k_{obsd} - k_{un} = -K_d \times (k_{obsd} - k_{un})/[3] + (k_{conn} - k_{un})$. Since (as can be seen from Figure 1) there were small variations in the pressure at which the various concentrations of **3** were run, the k_{obsd} values used are those resulting from intrapolations. The pressure dependences of k_{com} and K_d are assessed by means of least-square fits of $\ln k = a + bp + cp^2$, giving ΔV^*_{com} and ΔV_d from $\Delta V^{(*)} = -bRT$; finally ΔV^*_{com} is corrected for the volume change (-1.8 cm^3/mol) caused by the pressure-induced shift in the buffer equilibrium.

Acknowledgment. This work was supported by the N.S.F at Stony Brook and the N.I.H. at Columbia. G.T. expresses appreciation for his N.I.H. postdoctoral fellowship.

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New Aspects of the Telluroxide Elimination. A Facile Elimination of *sec*-Alkyl Phenyl Telluroxide Leading to Olefins, Allylic Alcohols, and Allylic Ethers

Sakae Uemura* and Shin-ichi Fukuzawa

Contribution from the Institute for Chemical Research, Kyoto University, Uji, Kyoto 611, Japan. *Received September 28, 1982*

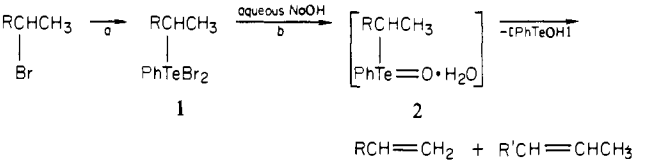
Abstract: The utility of the telluroxide for olefin synthesis, a reaction which previously appeared to be of little value, is described. Treatment of *sec*-alkylphenyltellurium dibromides, except for the cyclohexyl system, with aqueous NaOH at room temperature affords olefins, allylic alcohols, and/or allylic ethers in high yields presumably via the formation of *sec*-alkyl phenyl telluroxides and their facile telluroxide elimination. As to the formation of linear olefins, more preference for elimination toward the less substituted carbon was observed than the selenoxide and sulfoxide eliminations. In the cyclododecyl case only *trans*-cyclododecene was formed as an olefin component in a sharp contrast to the selenoxide elimination that affords a 1:1 mixture of cis and trans isomers. On the contrary, in the *n*-alkyl and cyclohexyl cases the corresponding telluroxides are stable compounds that afford similar elimination products including vinylic ethers only by neat pyrolysis at temperatures above 200 °C.

In contrast to the well-known selenoxide elimination leading to double-bond formation,[1] little is known on the telluroxide elimination.[2] On this subject only two reports have so far appeared to our knowledge. Original work has been done by Sharpless et al.,[3] who reported the formation of mixtures of olefins and/or alcohols by *tert*-butyl hydroperoxide oxidation of several tellurides in benzene without isolation of the telluroxides. Recently, Cava et al.[4] clarified that *n*-dodecyl 4-methoxyphenyl telluroxide is stable and its decomposition to 1-dodecene and the corresponding telluride occurs only in refluxing CCl_4 or toluene for a longer time. We have found that it is not necessarily the case for all telluroxides and, in fact, *sec*-alkyl phenyl telluroxides decompose readily to afford olefins, allylic alcohols, and allylic ethers in high yields under very mild conditions. In this paper we would like to report on the utility of the telluroxide for olefin and allylic compound syntheses, a reaction which previously appeared to be of little value.

Results and Discussion

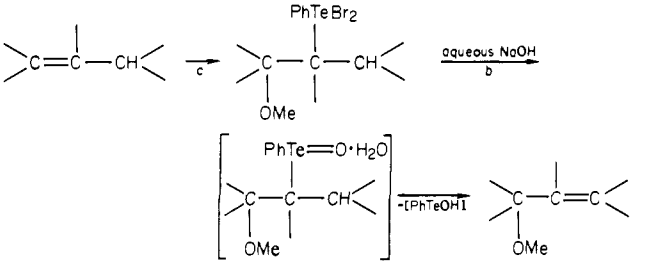
When we tried to prepare *sec*-octyl phenyl telluroxide (or its hydrate) (**2**, R = *n*-C_6H_{13}) by treating the corresponding stable dibromide (**1**, R = *n*-C_6H_{13}) with aqueous NaOH at room temperature,[5] the expected compound could not be isolated and instead a mixture of 1-octene and *trans*- and *cis*-2-octenes was obtained in a yield of 80% together with small amounts of 2-octanol and 2-octanone (Scheme I, Table I).[6] Similar facile telluroxide elimination was also observed to give the corresponding olefins in a yield of over 70% by starting from 2-dodecyl, 2-tetradecyl, cycloheptyl, cyclooctyl, and cyclododecyl bromides, small amounts of the corresponding alcohol and ketone being detected in all cases.[7]

Scheme I



conditions: a, $(PhTe)_2/NaBH_4/EtOH$ (reflux for 1-5 h) and Br_2/CCl_4 (0 °C); b, aqueous 0.5 N NaOH (20-25 °C for 1-3 h)

Scheme II



condition: c, $(PhTe)_2/Br_2$ or $PhTeBr_3$ in MeOH (reflux for 1-2 h)

(1) For a review, see: (a) Reich, H. J. "Oxidation in Organic Chemistry, Part C"; Trahanovsky, W.; Ed.; Academic Press: New York, 1978; pp 1-130. (b) Clive, D. L. J. *Tetrahedron* **1978**, *34*, 1049. (c) Reich, H. J. *Acc. Chem. Res.* **1979**, *12*, 22.

(2) Uemura, S. *Kagaku (Kyoto)* **1981**, *36*, 381.

(3) Sharpless, K. B.; Gordon, K. M.; Lauer, R. F.; Patrick, D. W.; Singer, S. P.; Young, M. W. *Chem. Scr.* **1975**, *8A*, 9.

(4) Lee, H.; Cava, M. P. *J. Chem. Soc., Chem. Commun.* **1981**, 277.

(5) Detty, M. J. *J. Org. Chem.* **1980**, *45*, 274. The method is known to be the best one for the preparation of the telluroxide that is not contaminated by the corresponding tellurone.

(6) An eliminated phenyltellurenic acid (PhTeOH) was detected partly as diphenyl ditelluride that is probably formed by the following disproportionation and oxidation reactions (see Experimental Section).

$$2PhTeOH \rightarrow PhTeOOH + PhTeH$$

$$2PhTeH \xrightarrow{[O]} (PhTe)_2 + H_2O$$

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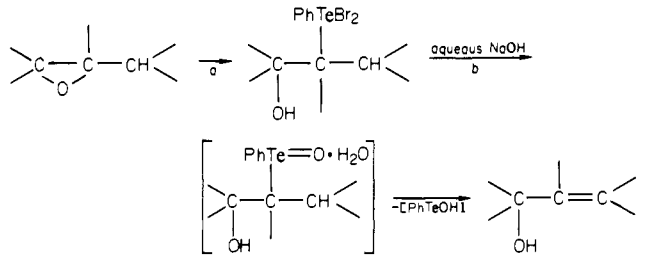
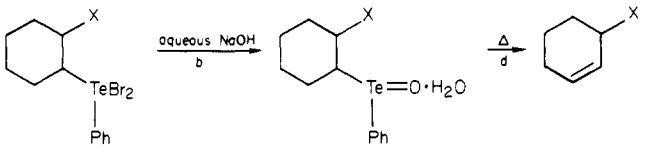
Scheme III



Scheme IV



3 4, X = H and OMe

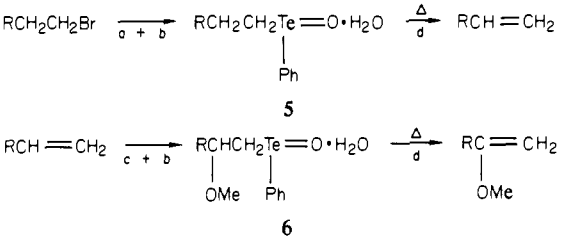
condition: d, Kugelrohr distillation at 200–240 °C (20–760 torr)

As to the formation of linear olefins, the ratio of terminal to internal olefins observed here when R = *n*-C_6H_{13} and *n*-C_8H_{17} (2.48–2.50/1) is higher than that observed in the selenoxide[8] and sulfoxide[9] eliminations of 2-butyl phenyl selenoxide (1.56/1) and its sulfoxide analogue (1.5/1), respectively.[10] Namely, the telluroxide elimination shows more preference for elimination toward the less substituted carbon than the selenoxide and sulfoxide eliminations where the ratio of terminal to internal olefins seems to be governed statistically by the number of hydrogen (CH_3 vs. CH_2).[1a] In the cyclododecyl case only *trans*-cyclododecene was formed as an olefin component in a sharp contrast to the selenoxide elimination that affords a 1:1 mixture of cis and trans isomers.[8]

When this procedure was combined with the recently reported method for the oxytelluration of olefins with use of $(PhTe)_2/Br_2$ or $PhTeBr_3$ as an electrophilic tellurium reagent,[11] allylic ethers were readily obtained from such internal olefins as *trans*-4-octene, cycloheptene, and cyclooctene (Scheme II, Table I). Similarly, allylic alcohols were obtained from (β-hydroxyalkyl)tellurium compounds that are prepared by ring opening of the corresponding epoxides (Scheme III, Table I).[12] The stereochemistry at the double bond of the produced linear allylic methyl ether and allylic alcohol was revealed to be completely trans by ^1H NMR spectroscopy.

Quite interestingly, the cyclohexyl system was revealed to be exceptional. Thus, cyclohexyl and 2-methoxycyclohexyl phenyl telluroxides (or their hydrates) (**4**, X = H and OMe) were isolated, respectively, as very stable compounds by treating the corresponding dibromides (**3**) with aqueous NaOH at room temperature, and the telluroxide elimination hardly occurred under this condition (Scheme IV). In these cases the pyrolysis using Kugelrohr distillation apparatus at 200–220 °C gave the expected cyclohexene and 3-methoxycyclohexene, respectively. Such an unusual stability of cyclohexane derivatives has precedents in 2-acetamidocyclohexyl[13] and 2-hydroxycyclohexyl phenyl selenoxides,[5,14] but in these cases the stability was attributed to an intramolecular hydrogen bonding. The isolation of (**4**, X = H and OMe), where no such intramolecular interaction for stabilization is expected, therefore, suggests that in the telluroxide case the cyclohexyl compounds themselves may be conformationally stable.

Scheme V

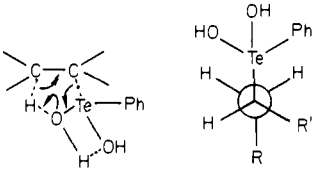


5

6

Contrary to observations for the above described *sec*-alkyl phenyl telluroxides *n*-alkyl analogues such as **5** and **6**, prepared by a similar way as above, were revealed to be stable compounds as reported by Cava et al.[4] We found that the pyrolysis of these by Kugelrohr distillation apparatus at 200–240°C afforded the corresponding olefins and vinylic ethers in good yields (Scheme V, Table I).

It has been established that the elimination of telluride by *t*-BuOOH oxidation (presumed to occur via telluroxide) occurs mainly by syn elimination.[3] This means that telluroxide elimination proceeds via internal elimination (E_i) as in the case of the selenoxide. Our observation of a great reactivity difference for elimination between secondary and primary alkyl telluroxides may suggest that the C–Te bond fission by electron flow from C to Te is an important step for this E_i elimination in a transition state [A] that is shown in the form of dihydroxytellurane, because the



[A] [B], R' = H, alkyl

stability of a carbonium ion may then decide the rate of elimination. The difference in steric crowding between both telluroxides (R' = H and alkyl in [B]) may also play a role, telluroxide elimination from [B, R' = alkyl] being expected to be more favorable. Selenoxide elimination is a more favorable process than telluroxide elimination, and yet it has been observed that the yield of olefins produced by oxidation of alkyl phenyl selenide was generally lower in the case of primary alkyl compounds that in the case of secondary analogues,[1,15] suggesting also a higher stability of the former than the latter.

The reason for the telluroxides' lesser reactivity for elimination compared to the selenoxides seems to be as follows. (1) All the "telluroxides" were isolated as their hydrates and are almost certainly dihydroxytelluranes in which the tellurium is four-coordinate as shown in [A] and [B]. In this form the basicity of oxygen for hydrogen may be reduced and the elimination should be slower compared to the selenoxides, which have a smaller tendency to add water. (2) The longer bond lengths (C–M and M–O, M = Te, Se) in telluroxide than in selenoxide may place the oxygen far away from the appropriate hydrogen to be eliminated as has been proposed by Sharpless et al.[3]

Experimental Section

^1H NMR spectra were taken 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 (JNM FX-

(7) An alcohol may be formed by 1,2-shift reaction of the telluroxide as proposed by Sharpless et al.,[3] while a ketone may be derived from the produced alcohol.

(8) Sharpless, K. B.; Young, M. W.; Lauer, R. F. *Tetrahedron Lett.* **1973**, 1979.

(9) Shelton, J. R.; Davis, K. E. *Int. J. Sulfur Chem.* **1973**, *8*, 197.

(10) It has been reported recently that alkyl phenyl tellurides reacted with chloramine-T in THF under reflux to give olefins, the ratio of terminal to internal olefins being reported to be 2.2 when alkyl is 2-tetradecyl. Otsubo, T.; Ogura, F.; Yamaguchi, H.; Higuchi, H.; Sakata, Y.; Misumi, S. *Chem. Lett.* **1981**, 447.

(11) Uemura, S.; Fukuzawa, S.; Toshimitsu, A.; Okano, M. *Tetrahedron Lett.* **1982**, *23*, 1177.

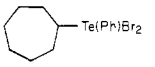
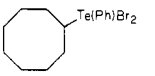
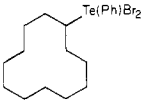
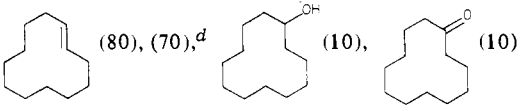
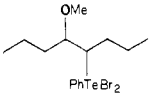
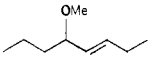
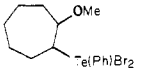
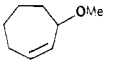
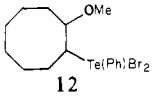
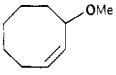
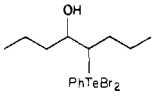
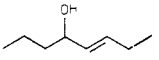
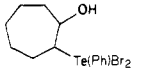
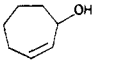
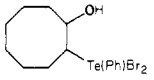
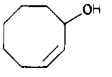
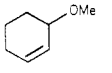
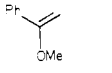
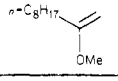
(12) Clive, D. L. J.; Chittattu, G. J.; Farina, V.; Kiel, W. A.; Menchen, S. M.; Russell, C. G.; Singh, A.; Wong, C. K.; Curtis, N. J. *J. Am. Chem. Soc.* **1980**, *102*, 4438.

(13) Toshimitsu, A.; Aoai, T.; Owada, H.; Uemura, S.; Okano, M. *J. Org. Chem.* **1981**, *46*, 4727.

(14) Rickards, R. W.; Watson, W. P. *Aust. J. Chem.* **1980**, *33*, 451.

(15) Toshimitsu, A.; Owada, H.; Uemura, S.; Okano, M. *Tetrahedron Lett.* **1980**, *21*, 5037.

Table I. Telluroxide Elimination Leading to Olefins, Allylic Alcohols, Allylic Ethers, and Vinylic Ethers[a]

starting compd	conditn for telluratn	Te compd (isolated yield, %)	conditn for eliminatn	product (yield, %)[b]
2-bromooctane	a	**1**, R = *n*-C_6H_{13} (80)	b	1-octene (57), *trans*-2-octene (19), *cis*-2-octene (4), 2-octanol (10), 2-octanone (10)
2-bromodecane	a	**1**, R = *n*-C_8H_{17} (90)	b	1-decene (50), 2-decenes (20),[c] 2-decanol (2), 2-decanone (3)
2-bromotetradecane	a	**1**, R = *n*-$C_{12}H_{25}$ (90)	b	1- and 2-tetradecenes (80), 2-tetradecanone (4), 2-tetradecanol (3)
bromocyclohexane	a + b	**4**, X = H (80)	d	cyclohexene (72), cyclohexanol (2), cyclohexanone (trace)
bromocycloheptane	a	 (78) **7**	b	cycloheptene (70), cycloheptanol (3), cycloheptanone (10)
bromocyclooctane	a	 (67) **8**	b	cyclooctene (70), cyclooctanol (9), cyclooctanone (20)
bromocyclododecane	a	 (77) **9**	b	 (80), (70),[d] (10), (10)
1-bromododecane	a + b	**5**, R = *n*-$C_{10}H_{21}$ (100)	d	1-dodecene (50), 1-dodecanol (11)
trans-4-octene	c	 (20) **10**	b	 (80)[d]
cycloheptene	c	 (52) **11**	b	 (99), (70)[d]
cyclooctene	c[e]	 (42) **12**	b	 (81)[d]
trans-4-octene oxide	a	 (71) **13**	b	 (78)[d]
cycloheptene oxide	a	 (70) **14**	b	 (67)[d]
cyclooctene oxide	a	 (80) **15**	b	 (67)[d]
cyclohexene	c + b	**4**, X = OMe (60)	d	 (70)[d]
styrene	c + b	**6**, R = Ph (58)	d	 (56)[d]
1-decene	c + b	**6**, R = *n*-C_8H_{17} (66)	d	 (78)[d]

[a] Reaction conditions: a, $(PhTe)_2/NaBH_4/EtOH$ (reflux for 1–5 h) and Br_2/CCl_4 (0 °C); b, aqueous 0.5 N NaOH (20–25 °C for 1–3 h); c, $(PhTe)_2$–Br_2 or $PhTeBr_3$/MeOH (reflux for 1–2 h); d, pyrolysis by Kugelrohr distillation apparatus (200–240 °C at 20–760 torr). [b] GLPC yield with internal standard. [c] A cis/trans mixture. [d] Isolated yield. [e] Reflux for 12 h.

100) 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 by using a Shimadzu 4CMPF apparatus using Silicone QF-1(5%)-Chromosorb-W (1 m), PEG 6000(25%)-Shimalite (1 and 3 m), and EGSS-X(15%)-Chromosorb-W (1 m) columns (N_2 as carrier gas). IR spectra were recorded with Perkin-Elmer 521 (4000–250 cm^{-1}) and Hitachi FIS-3 (400–30 cm^{-1}) spectrometers (KBr disk, neat, and paraffin mulls). Mass spectra were measured on a JEOL JMS-DX 300 mass spectrometer, equipped with a JMA-3500 data processing system. The ionization voltage was 70 eV for all compounds. Melting points were determined with Shimadzu MM-2 micro melting point determination apparatus and were uncorrected.

Diphenyl ditelluride was prepared by the reported method from Te and PhMgBr.[16] Commercially available Te, magnesium turnings, $NaBH_4$, and Br_2 (Wako Pure Chemical) were used without further pu-

(16) Haller, W. S.; Irgolic, K. J. *J. Organomet. Chem.* **1972**, *38*, 97.

rification, while commercial organic compounds were distilled immediately before use. Detelluration products such as olefins, alcohols, and ketones except 2-decenes, 2-tetradecenes, 2-cycloocten-1-ol, and 2-tetradecanone are commercially available for GLC analyses. 2-Decenes and 2-tetradecenes were prepared respectively as a cis/trans mixture by the Wittig reaction between triphenylphosphine ethylidene and the corresponding 1-aldehydes.[17] 2-Cycloocten-1-ol was prepared by the reported method,[18] while 2-tetradecanone was prepared by the Jones oxidation of 2-tetradecanol. Allylic and vinylic methyl ethers, 2-cyclohepten-1-ol, and 3-octen-5-ol were isolated by distillation and identified by ^{1}H NMR spectroscopy.

Preparation of *sec*-Alkylphenyltellurium Dibromide (1). General Procedure (Condition a). To a suspension of 2.05 g (5 mmol) of diphenyl ditelluride in 20 mL of anhydrous ethanol was added 0.41 g (11 mmol) of solid sodium borohydride at 20 °C under N_2 with stirring.[12] 2-Bromooctane (1.92 g, 10 mmol) was then added to the resulting homogeneous pale yellow solution, and the mixture was stirred for 3 h under reflux, followed by cooling to room temperature. Water (150 mL) was added, and the products were extracted with $CHCl_3$ (50 mL × 3). The organic layer was washed with brine and dried over $MgSO_4$. Removal of the solvent under reduced pressure left an oily residue, which was chromatographed on silica gel (elution with hexane), providing 2-octyl phenyl telluride as a yellow oil. To a CCl_4 (10 mL) solution of this oil was added dropwise a CCl_4 (10 mL) solution of 1.6 g (10 mmol) of bromine at 0 °C. Evaporation of the solvent in vacuo provided 3.82 g of pure 2-octylphenyltellurium dibromide (**1**, R = *n*-C_6H_{13}) as a yellow oil: ^{1}H NMR (100 MHz) δ 0.7–1.7 (m, 11 H), 1.78 (d, 3 H), 1.9–2.4 (m, 2 H), 4.36 (sext, 1 H), 7.4–7.6 (m, 3 H), 8.15–8.4 (m, 2 H); ^{13}C NMR δ 13.9 (q), 18.0 (q), 22.4 (t), 28.6 (t), 28.9 (t), 31.4 (t), 34.4 (t), 62.2 (d, CHTe), 125.2 (s), 129.9 (d), 131.4 (d), 135.4 (d). Anal. Calcd for $C_{14}H_{22}Br_2Te$: C, 35.20; H, 4.64. Found: C, 34.80; H, 4.81.

1 (R = *n*-C_8H_{17}): a yellow oil; ^{1}H NMR (60 MHz) δ 0.8–1.6 (m, 15 H), 1.74 (d, 3 H), 1.8–2.3 (m, 2 H), 4.28 (sext, 1 H), 7.2–7.5 (m, 3 H), 8.0–8.3 (m, 2 H). Anal. Calcd for $C_{16}H_{26}Br_2Te$: C, 37.99; H, 5.18. Found: C, 37.84; H, 5.41.

1 (R = *n*-$C_{12}H_{25}$): a yellow oil; ^{1}H NMR (60 MHz) δ 0.8–1.4 (m, 23 H), 1.72 (d, 3 H), 1.9–2.4 (m, 2 H), 4.25 (sext, 1 H), 7.3–7.5 (m, 3 H), 8.0–8.3 (m, 2 H). Anal. Calcd for $C_{20}H_{34}Br_2Te$: C, 42.75; H, 6.10. Found: C, 42.95; H, 6.36.

Cyclohexylphenyltellurium dibromide (3, X = H): a pale yellow needle, mp 117 °C (hexane–$CHCl_3$); IR (KBr) 2940, 2850, 1570, 1470, 1448, 1438 (s), 1328, 1296, 1256, 1250, 1173 (s), 1090, 1060, 1050, 1010, 988 (s), 883, 730 (s), 676, 640, 450 cm^{-1}; ^{1}H NMR (60 MHz) δ 1.0–2.3 (m, 10 H), 4.31 (quint, 1 H), 7.3–7.6 (m, 3 H), 8.0–8.3 (m, 2 H). Anal. Calcd for $C_{12}H_{16}Br_2Te$: C, 32.20; H, 3.60. Found: C, 31.90; H, 3.60.

Cycloheptylphenyltellurium dibromide (7): a yellow oil; ^{1}H NMR (100 MHz) δ 1.3–2.5 (m, 12 H), 4.24 (tt, 1 H, *J* = 10, 4.9 Hz), 7.4–7.6 (m, 3 H), 8.1–8.4 (m, 2 H); ^{13}C NMR δ 27.1 (t), 28.2 (t), 32.0 (t), 66.3 (d, CHTe), 126.9 (s), 130.0 (d), 131.4 (d), 135.1 (d). Anal. Calcd for $C_{13}H_{18}Br_2Te$: C, 33.82; H, 3.93. Found: C, 34.09; H, 4.18.

Cyclooctylphenyltellurium dibromide (8): a yellow oil; ^{1}H NMR (60 MHz) δ 1.5–2.6 (m, 14 H), 4.40 (quint, 1 H), 7.3–7.6 (m, 3 H), 8.0–8.4 (m, 2 H). Anal. Calcd for $C_{14}H_{20}Br_2Te$: C, 35.35; H, 4.24. Found: C, 35.07; H, 4.28.

Cyclododecylphenyltellurium dibromide (9): a white solid, mp 120 °C (hexane–$CHCl_3$); ^{1}H NMR (60 MHz) δ 1.2–2.5 (m, 22 H), 4.0–4.8 (m, br, 1 H), 7.2–7.6 (m, 3 H), 8.0–8.3 (m, 2 H); mass spectrum, *m/e* (relative intensity, only peaks stronger than 15% of the base peak above *m/e* 350) 455 (21), 453 (38), 451 (32), 449 (16), 414 (27), 412 (47), 410 (55), 408 (35), 406 (20), 375 (22), 374 (100), 373 (17), 372 (93), 370 (57), 369 (26). Anal. Calcd for $C_{18}H_{28}Br_2Te$: C, 40.65; H, 5.31. Found: C, 40.32; H, 5.38.

Preparation of (β-Methoxyalkyl)phenyltellurium Dibromide. Methoxytelluration of Olefins.[11] General Procedure (Condition c). To a MeOH (5 mL) solution of 2.23 g (5 mmol) of phenyltellurium tribromide,[19] prepared from diphenyl ditelluride and bromine, was added 0.82 g (10 mmol) of cyclohexene, and the mixture was heated under reflux for 1 h. When the resulting yellow homogeneous solution was cooled to room temperature, the pale yellow (2-methoxycyclohexyl)-phenyltellurium dibromide (**3**, X = OMe) (1.46 g, 3.05 mmol, 61% yield) was precipitated, filtered off, and washed with a small amount of chilled MeOH: mp 180–181 °C; IR (KBr) 2948, 2920, 2860, 2820, 1566, 1476, 1450 (s), 1438 (s), 1360, 1342, 1330, 1320, 1310, 1280, 1248, 1183 (s), 1160, 1099 (s), 1084 (s), 1051, 997, 941, 928, 898, 856, 838, 739 (s), 680, 647, 523, 478, 450, 400, 370, 325, 270, 253, 240, 216, 170 (s), 135, 105 cm^{-1}; ^{1}H NMR (60 MHz) δ 1.0–2.2 (m, 8 H), 3.45 (s, 3 H), 3.8–4.4 (m, 2 H), 7.2–7.6 (m, 3 H), 8.2–8.4 (m, 2 H); ^{13}C NMR δ 23.4 (t), 27.5 (t), 27.5 (t), 31.7 (t), 56.3 (q), 71.5 (d, CHTe), 75.6 (d), 124.1 (s), 129.3 (d), 130.8 (d), 136.1 (d). Anal. Calcd for $C_{13}H_{18}Br_2OTe$: C, 32.69; H, 3.80. Found: C, 32.54; H, 3.55.

Spectral and analytical data of methoxytelluration products of other olefins such as **10–12** in Table I will be reported separately in a full account of the preliminary communication.[11]

Preparation of (β-Hydroxyalkyl)phenyltellurium Dibromide. General Procedure (Condition a). Almost the same procedure as in the preparation of **1** was applied to various epoxides[12] in the place of alkyl bromides except that the product β-hydroxyalkyl phenyl telluride was chromatographed on silica gel using hexane–ethyl acetate (5:1) as eluent.

[4-(5-Hydroxyoctyl)]phenyltellurium dibromide (13): a yellow syrup: ^{1}H NMR (60 MHz) δ 0.7–2.5 (m, 14 H), 2.9 (br s, 1 H, OH), 4.3–4.7 (m, 2 H), 7.3–7.6 (m, 3 H), 8.0–8.4 (m, 2 H). Anal. Calcd for $C_{14}H_{22}Br_2OTe$: C, 34.13; H, 4.30. Found: C, 34.58; H, 4.71.

(2-Hydroxycyclohexyl)phenyltellurium dibromide: a pale yellow solid, mp 104–105 °C; ^{1}H NMR (60 MHz) δ 1.0–2.4 (m, 8 H), 2.9 (br s, 1 H, OH), 4.0–4.4 (br, 2 H), 7.3–7.6 (m, 3 H), 8.0–8.4 (m, 2 H). Anal. Calcd for $C_{12}H_{16}Br_2OTe$: C, 31.08; H, 3.48. Found: C, 31.14; H, 3.60. For comparison, ^{1}H NMR (60 MHz) spectrum of 2-hydroxycyclohexyl phenyl telluride: δ 1.0–2.3 (m, 8 H), 2.6 (br s, 1 H, OH), 3.1–3.4 (br, 2 H), 7.0–7.3 (m, 3 H), 7.6–7.8 (m, 2 H).

(2-Hydroxycycloheptyl)phenyltellurium dibromide (14): a pale yellow syrup; ^{1}H NMR (60 MHz) δ 1.0–2.2 (m, 10 H), 3.6 (br s, 1 H, OH), 4.0–4.5 (m, 2 H), 7.0–7.4 (m, 3 H), 7.9–8.3 (m, 2 H). Anal. Calcd for $C_{13}H_{18}Br_2OTe$: C, 32.69; H, 3.80. Found: C, 33.23; H, 4.01.

(2-Hydroxycyclooctyl)phenyltellurium dibromide (15): a yellow syrup; IR (neat) 3550 (s), 3070, 2940 (s), 2870, 1572, 1473, 1434, 1370, 1300, 1260 (s), 1045, 998, 735 (s), 684 cm^{-1}; ^{1}H NMR (60 MHz) δ 1.0–2.5 (m, 12 H), 3.0 (br s, 1 H, OH), 4.0–4.8 (m, 2 H), 7.3–7.6 (m, 3 H), 8.0–8.4 (m, 2 H). Anal. Calcd for $C_{14}H_{20}Br_2OTe$: C, 34.20; H, 4.10. Found: C, 35.00; H, 4.40.

Telluroxide Elimination. General Procedure (Condition b). To a colorless THF (20 mL) solution of **9** (0.53 g, 1.0 mmol) was added aqueous 0.5 N NaOH (10 mL) at 20 °C under stirring. The resulting solution was stirred for 1 h, during which period the color of the solution turned to orange. The reaction mixture was diluted with brine and then extracted with diethyl ether (30 mL × 3), the extract being dried over $MgSO_4$. GLC analysis of the extract [using 1-tetradecene (for olefin) and 2-tetradecanol (for alcohol and ketone) as internal standards] showed the presence of *trans*-cyclododecene (0.80 mmol, 80% yield), cyclododecanol (10%), and cyclododecanone (10%). Removal of the solvent under reduced pressure left an oily orange residue, which was chromatographed on silica gel (elution with hexane), providing 0.1 g (0.24 mmol) of diphenyl ditelluride. By distillation of the extract obtained from the reaction using 1.06 g (2.0 mmol) of **9**, 0.23 g (1.40 mmol, 70% yield), of pure *trans*-cyclododecene was isolated: IR (neat) 2940 (s), 2870 (s), 2690, 1460 (s), 1445 (s), 1346, 1295, 1230, 1096, 1058, 975 (s), 726, 718, 696 cm^{-1}; ^{1}H NMR (100 MHz) δ 1.0–1.6 (m, 16 H), 1.75–2.15 (m, 4 H), 5.38 (tt, 2 H, *J* = 4.2, 2 Hz).

5-Methoxy-3-octene: ^{1}H NMR (100 MHz) δ 0.8–1.2 (m, 6 H), 1.2–1.8 (m, 4 H), 1.9–2.2 (m, 2 H), 3.28 (s, 3 H), 3.40 (dt, 1 H), 5.20 (ddt, 1 H, *J* = 16, 8, 2 Hz), 5.60 (dt, 1 H, *J* = 16, 5 Hz).

3-Methoxycycloheptene: ^{1}H NMR (60 MHz) δ 1.3–2.3 (m, 8 H), 3.33 (s, 3 H), 3.8–4.0 (m, 1 H), 5.7–5.9 (m, 2 H).

3-Methoxycyclooctene: ^{1}H NMR (60 MHz) δ 1.1–2.4 (m, 10 H), 3.29 (s, 3 H), 4.0–4.2 (m, 1 H), 5.4–5.6 (m, 2 H).

3-Octen-5-ol: ^{1}H NMR (100 MHz) δ 0.8–1.2 (m, 6 H), 1.2–1.7 (m, 4 H), 1.8–2.2 (m, 2 H), 1.85 (br s, 1 H, OH), 4.08 (dt, 1 H), 5.42 (ddt, 1 H, *J* = 16, 6, 1.5 Hz), 5.71 (dt, 1 H, *J* = 16, 5.5 Hz).

2-Cyclohepten-1-ol: ^{1}H NMR (60 MHz) δ 1.0–2.2 (m, 8 H), 3.7 (br s, 1 H, OH), 4.1–4.3 (m, 1 H), 5.4–5.6 (m, 2 H).

Preparation of Telluroxide. General Procedure (Condition a + b or c + b). To a pale yellow THF (20 mL) solution of **3** (X = H) (0.75 g, 1.6 mmol) was added aqueous 0.5 N NaOH (10 mL) at 20 °C under stirring. After 1 h, during which period no color change was observed, the reaction mixture was diluted with distilled water and then extracted with diethyl ether (30 mL × 3). The extract was dried over $MgSO_4$, and then evaporation of the solvent in vacuo left a white solid of cyclohexyl phenyl telluroxide hydrate (**4**, X = H) (0.50 g, 100% yield): mp > 140 °C dec; IR (KBr) 3330 (s, br), 3050, 2930 (s), 2852 (s), 1568, 1478, 1450 (s), 1437 (s), 1328, 1253, 1175, 1058, 1020, 990, 912, 882, 840, 738 (s), 690 (s), 640 (s), 576 (s), 467, 458, 420, 380 cm^{-1}; ^{1}H NMR (100 MHz) δ 0.8–2.6 (m, 10 H), 2.8–4.2 (m, 3 H), 7.0–7.8 (m, 3 H), 7.8–8.6 (m, 2 H). Anal. Calcd for $C_{12}H_{16}OTe{\cdot}H_2O$: C, 44.78; H, 5.64. Found: C, 45.17; H, 5.50.

(17) Wittig, G.; Schoellkopf, U. "Organic Syntheses"; Wiley: New York, 1973; Coll. Vol. 5, p 751.
(18) Cope, A. C.; Kinter, M. R.; Keller, R. T. *J. Am. Chem. Soc.* **1954**, *76*, 2757.
(19) McWhinnie, W. R.; Thavornyutikarn, P. *J. Chem. Soc., Dalton Trans.* **1972**, 551.

All other telluroxides were similarly prepared from the corresponding dibromides.

2-Methoxycyclohexyl phenyl telluroxide hydrate (4, X = OMe): a white solid, mp > 100 °C dec; IR (KBr) 3420 (s, br), 3050, 2940, 2860, 1630, 1575, 1475, 1450, 1439, 1363, 1250, 1185, 1102 (s), 1090 (sh), 1008, 1000, 929, 858, 840, 738 (s), 690 (s), 580 (s, br), 453, 115 (br) cm^{-1}; ^1H NMR (100 MHz) δ 0.8-1.9 (m, 8 H), 2.2 (br s, 1 H), 2.7-3.8 (m, 3 H), 3.32 (s, 3 H), 7.2-7.5 (m, 3 H), 7.8-8.2 (m, 2 H); ^{13}C NMR δ 23.7 (t), 25.5 (t), 26.7 (t), 31.4 (t), 55.5 (q), 77.6 (d), 79.4 (d), 128.8 (d), 130.2 (d), 132.5 (d), 133.3 (s). Anal. Calcd for $C_{13}H_{18}O_2Te \cdot H_2O$: C, 44.37; H, 5.73. Found: C, 44.80; H, 5.20.

***n*-Dodecyl phenyl telluroxide hydrate (5, R = *n*-$C_{10}H_{21}$)**: a colorless syrup; IR (neat) 3400 (br), 3075, 2945 (s), 2880 (s), 1575, 1466 (s), 1433 (s), 1374, 1304, 1180, 1095 (br s), 1035 (br s), 1020 (sh), 998, 995, 910, 735 (s), 688 (s) cm^{-1}; ^1H NMR (60 MHz) δ 0.5-1.5 (m, 23 H), 1.8-2.3 (br, 1 H), 2.5-3.7 (br, m, 3 H), 6.8-7.5 (m, 3 H), 7.5-8.4 (m, 2 H). Anal. Calcd for $C_{18}H_{30}OTe \cdot H_2O$: C, 52.98; H, 7.90. Found: C, 52.42; H, 7.65.

2-Methoxy-2-phenylethyl phenyl telluroxide hydrate (6, R = Ph): a colorless solid, mp 82-84 °C; IR (KBr) 3350 (br), 3070, 2940, 1574, 1490, 1473, 1452, 1434, 1395, 1355, 1305 (br), 1222, 1133, 1095 (s), 1020, 998, 935, 840, 760, 737 (s), 700 (s), 690 cm^{-1}; ^1H NMR (60 MHz) δ 2.65-3.7 (m, 4 H), 3.17 (s, 3 H), 4.80 (t, 1 H), 7.0-7.55 (m, 8 H), 7.9-8.3 (m, 2 H). Anal. Calcd for $C_{15}H_{16}O_2Te \cdot H_2O$: C, 48.18; H, 4.85. Found: C, 48.53; H, 4.61.

2-Methoxydecyl phenyl telluroxide hydrate (6, R = *n*-C_8H_{17}): a colorless syrup: IR (neat) 3400 (br), 3060, 2940 (s), 2870 (s), 1465, 1432, 1370, 1095 (br, s), 736, 688 cm^{-1}; ^1H NMR (60 MHz) δ 0.65-1.6 (m, 17 H), 2.5-4.0 (m, 5 H), 3.25 (s, 3 H), 7.0-7.4 (m, 3 H), 7.7-8.0 (m, 2 H). Anal. Calcd for $C_{17}H_{28}O_2Te \cdot H_2O$: C, 49.80; H, 7.37. Found: C, 49.58; H, 7.46.

Thermal Fragmentation of Alkyl Phenyl Telluroxide Hydrate (Condition d). Pyrolysis of **6** (R = Ph) (0.89 g, 2.5 mmol) was carried out by using Kugelrohr distillation apparatus at 200-240 °C (20 torr) to afford 0.188 g (1.40 mmol, 56%) of α-methoxystyrene as an oil: ^1H NMR (60 MHz) δ 3.64 (s, 3 H), 4.11 (d, 1 H; J = 2.8 Hz), 4.55 (d, 1 H, J = 2.8 Hz), 7.15 (m, 3 H), 7.42 (m, 2 H).

Pyrolysis of **4** (X = OMe) and **6** (R = *n*-C_8H_{17}) was similarly carried out to give 3-methoxycyclohexene [^1H NMR (60 MHz) δ 1.3-2.2 (m, 6 H), 3.34 (s, 3 H), 3.72 (m, 1 H), 5.74 (m, 2 H)] and 2-methoxy-1-decene [^1H NMR (60 MHz) δ 0.85 (t, 3 H), 1.0-1.6 (m, 12 H), 1.9-2.2 (m, 2 H), 3.50 (s, 3 H), 3.83 (s, 2 H); ^{13}C NMR δ 54.6 (q, OCH_3), 79.9 (t, $=CH_2$), 164.6 (s, $=C(OMe)$)], respectively.

In the case of **4** (X = H) pyrolysis was carried out at 200-220 °C (760 torr), and the distillate was dissolved in hexane and analyzed by GLC.

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Registry No. 1 (R = C_6H_{13}), 84988-02-3; **1** (R = C_8H_{17}), 84988-03-4; **1** (R = $C_{12}H_{25}$), 83486-08-2; **3** (X = OH), 84988-18-1; **3** (X = H), 84988-17-0; **3** (X = OMe), 82486-31-5; **4** (X = H), 84988-04-5; **4** (X = OMe), 82486-30-4; **5** (R = $C_{10}H_{21}$), 84988-08-9; **6** (R = Ph), 84988-15-8; **6** (R = C_8H_{17}), 84988-16-9; **7**, 84988-05-6; **8**, 84988-06-7; **9**, 84988-07-8; **10**, 84988-09-0; **11**, 84988-10-3; **12**, 84988-11-4; **13**, 84988-12-5; **14**, 84988-13-6; **15**, 84988-14-7; 5-methoxy-3-octene, 55668-15-0; 3-methoxy-1-cycloheptene, 31059-39-9; 3-methoxy-1-cyclooctene, 26819-54-5; 5-hydroxy-3-octene, 58856-11-4; 2-cyclohepten-1-ol, 4096-38-2; 2-cyclooctene-1-ol, 3212-75-7; 2-methoxy-1-decene, 54123-72-7; 2-bromooctane, 557-35-7; 2-bromodecane, 39563-53-6; 2-bromotetradecane, 74036-95-6; bromocyclohexane, 108-85-0; bromocycloheptane, 2404-35-5; bromocyclooctane, 1556-09-8; bromocyclododecane, 7795-35-9; 1-bromododecane, 143-15-7; *trans*-4-octene, 14850-23-8; cycloheptene, 628-92-2; cyclooctene, 931-88-4; *trans*-4-octene oxide, 1689-70-9; cycloheptene oxide, 286-45-3; cyclooctene oxide, 286-62-4; cyclohexene, 110-83-8; styrene, 100-42-5; 1-decene, 872-05-9; 1-octene, 111-66-0; *trans*-2-octene, 13389-42-9; *cis*-2-octene, 7642-04-8; 2-octanol, 123-96-6; 2-octanone, 111-13-7; *cis*-2-decene, 20348-51-0; *trans*-2-decene, 20063-97-2; 2-decanol, 1120-06-5; 2-decanone, 693-54-9; 1-tetradecene, 1120-36-1; 2-tetradecene, 1652-97-7; 2-tetradecanone, 2345-27-9; 2-tetradecanol, 4706-81-4; cyclohexanol, 108-93-0; cyclohexanone, 108-94-1; cycloheptanol, 502-41-0; cycloheptanone, 502-42-1; cyclooctanol, 696-71-9; cyclooctanone, 502-49-8; *trans*-cyclododecene, 1486-75-5; cyclododecanol, 1724-39-6; cyclododecanone, 830-13-7; 1-dodecene, 112-41-4; 1-dodecanol, 112-53-8; 3-methoxy-1-cyclohexene, 2699-13-0; α-methoxystyrene, 4747-13-1; diphenyl ditelluride, 32294-60-3; phenyltellurium tribromide, 36309-64-5.

Stereopopulation Control. 7. Rate Enhancement in the Lactonization of 3-(*o*-Hydroxyphenyl)propionic Acids: Dependence on the Size of Aromatic Ring Substituents

Michael M. King[†] and Louis A. Cohen*

Contribution from the Department of Chemistry, George Washington University, Washington, D.C. 20052, and Laboratory of Chemistry, National Institute of Arthritis, Diabetes, Digestive and Kidney Diseases, National Institutes of Health, Bethesda, Maryland 20205.
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Abstract: A series of 4,4-dimethyl-6-hydroxyhydrocoumarins was synthesized with various combinations of methyl and halogen groups at C-5 and C-7. The 5,7-difluoro compound was obtained by condensation of difluorohydroquinone with dimethylacrylic ester. Controlled chlorination of the parent phenolic lactone provided the 5- and 7-chloro isomers, in addition to the 5,7-dichloro product. On the other hand, bromination gave both the 5,7-dibromo and 7-bromo products, without trace of the 5-bromo isomer; finally, iodination gave only the 7-iodo product. These compounds were converted into 6-mesylates as protection against air oxidation of the hydroquinone system in alkaline media. The lactones were hydrolyzed in aqueous base, and the kinetics of relactonization were measured at 30 °C over a wide pH range. As previously shown for similar systems, lactonization is subject to both general acid and general base catalysis. After adjustment of the rate constants (k') for the electronic effects of ring substituents, the residual rate constants (k'') were found to increase with the size of the C-5 substituent, the value for bromine being 4800 times that for hydrogen. A plot of log k''_{cat} vs. the van der Waals radius of the substituent is linear, demonstrating the existence of a free energy continuum in the relationship between k'' for lactonization and the conformational mobility of the three-carbon side chain.

In earlier work on stereopopulation control, we had shown that the introduction of substituents (e.g., CH_3) at unique sites in **1** (Scheme I) has a strong accelerating effect on the rate constants for acid- or base-catalyzed lactonization (**2**, **3**).[1,2] Analogous

[†] George Washington University.
* Author to whom inquiries should be addressed at National Institutes of Health.

(1) (a) Milstien, S.; Cohen, L. A. *J. Am. Chem. Soc.* **1972**, *94*, 9158. (b) Caswell, M.; Schmir, G. L. *Ibid.* **1980**, *102*, 4815. (c) For paper VI in this series, see Borchardt, R. T.; Cohen, L. A. *Ibid.* **1973**, *95*, 8319.