techniques. Scattering factors for the atoms were taken from ref 48. An absorption correction was applied to the data. The hydrogen atoms of the phenyl rings were treated as rigid groups with C–H fixed at 1.08 Å, and the thermal parameters of these atoms were refined with two related values for each group. The hydrogen atoms of the oxodimethylenemethane ligand were located from a difference Fourier, for which the contribution of low-angle reflections was enhanced, and the positional and isotropic thermal parameters were refined independently. All other atoms were refined anisotropically. For final cycles, a weighting parameter, $g(0.00044)\omega \propto [1/(\sigma^2 F + gF^2)]$, was employed and gave the final residual indices $R = \sum(|F_o| - |F_c|)/\sum|F_o| = 0.0526$ and $R' = [\sum\omega(|F_o| - |F_c|)^2]^{1/2} = 0.0532$. The highest residual peak in the final difference Fourier map was ~1.5e at 1 Å from Pt. An analysis of the weighting scheme over $|F_o|$ and $(\sin\theta)/\lambda$ was satisfactory.

The values for the refined postional parameters for all of the atoms are provided in Table V. A full table of the interatomic distances and bond angles and their estimated standard deviations are given in the supplementary material. Tables of the refined temperature factors and the observed and calculated structure factors for the structure are also available as supplementary material.

Computational Details. The parameters used in the extended Hückel calculations[49] were taken from the literature.[50] The geometry used for **16** was taken from the experimental values for **17**[4] and that for **18** from the optimized ab initio values except that the Pd–P distance was fixed at 2.33 Å. The ab initio SCF calculations used the GAUSSIAN 82 program.[51] A relativistic effective core potential was used for the core electrons in Pd[52] (up to 4s) and P[53] (up to 3s). The basis sets used were double-ζ for the valence region and of the form (341,431,31) for Pd[52] and (21,21) for P.[53] The 3-21G basis[54] was used for the oxodimethylenemethane ligand and STO-3G[55] for the hydrogens on the PH_3 groups. A full geometry optimization was carried out on **16** under a C_s symmetry constraint and for **18** under C_{2v} symmetry except that in each case the P–H distances were held constant at 1.42 Å and the Pd–P–H angles at 123.1°. The total energies computed for optimized **16** and **18** were −331.57372 and −331.56362 hartrees, respectively. Single-point calculations were carried out by using frozen core second-order Møller–Plesset (MP2) perturbation theory[56] at the optimum geometries. The total energies were −332.27177 and −332.25914 hartrees for **16** and **18**, respectively.

Acknowledgment. T.A.A. thanks the Robert A. Welch Foundation, the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the National Science Foundation for a generous allocation of computer time at the Pittsburgh Supercomputing Center. R.D.W.K. acknowledges the SERC for funding and provision of high-field NMR facilities, Dr. O. W. Howarth (University of Warwick) and Miss M. Robinson (University of Leicester) for high-field NMR measurements, and Johnson Matthey plc for the generous loan of platinum metal salts.

Registry No. **5**, 105302-65-6; **5**·CH_2Cl_2, 121443-75-2; **16**, **18**, 121443-76-3; [Pt(*trans*-stilbene)$(PPh_3)_2$], 39697-14-8; *cis*-[PtCl$(CH_2C(O)CH_2Cl)(PPh_3)_2$], 121443-74-1; 3-chloro-1-(trimethylsilyl)propan-2-one, 71482-65-0.

Supplementary Material Available: Full tables of bond lengths and angles (Tables S1 and S2) and atomic thermal parameters (Table S3) for **5**·CH_2Cl_2 (5 pages); a listing of structure factors (Table S4) for **5**·CH_2Cl_2 (17 pages). Ordering information is given on any current masthead page.

---

(47) Sheldrick, G. M. SHELX 76; Program for crystal structure determination, University of Cambridge, 1976.

(48) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, 1975; Vol. 4.

(49) Hoffmann, R. *J. Chem. Phys.* **1963**, *39*, 1297. Ammeter, J. H.; Bürgi, H.-B.; Thibeault, J. C.; Hoffmann, R. *J. Am. Chem. Soc.* **1978**, *100*, 3686.

(50) Tatsumi, K.; Hoffmann, R.; Yamamoto, A.; Stille, J. K. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 1857.

(51) Binkley, J. S.; Frisch, M. J.; DeFrees, D. J.; Raghavachari, K.; Whiteside, R. A.; Schlegel, H. B.; Pople, J. A., Carnegie-Mellon Chemistry Publishing Unit, Pittsburgh, 1984.

(52) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 299.

(53) Wadt, W. R.; Hay, P. J. *J. Chem. Phys.* **1985**, *82*, 284.

(54) Binkley, J. S.; Pople, J. A.; Hehre, W. J. *J. Am. Chem. Soc.* **1980**, *102*, 939.

(55) Hehre, W. J.; Stewart, R. F.; Pople, J. A. *J. Chem. Phys.* **1969**, *51*, 2657.

(56) Pople, J. A.; Binkley, J. S.; Seeger, R. *Int. J. Quantum Chem. Symp.* **1976**, *10*, 1.

Alkoxytellurination of Olefins for the Preparation of Bis(β-alkoxyalkyl) Ditellurides and (β-Alkoxyalkyl)tellurium Trichlorides

Lars Engman

Department of Organic Chemistry, Royal Institute of Technology, S-100 44 Stockholm, Sweden

Received January 17, 1989

Bis(β-alkoxyalkyl) ditellurides (**1**) were obtained when terminal olefins were heated with tellurium dioxide in alcoholic aqueous hydrochloric acid and the products, without isolation, were reduced with sodium disulfite. Only Markovnikov addition to the double bond was observed. Olefins containing a suitably positioned hydroxy group afforded cyclic ethers formed via an intramolecular oxytellurination reaction. By treatment with sulfuryl chloride the ditellurides were converted in high yields to (β-alkoxyalkyl)tellurium trichlorides.

Introduction

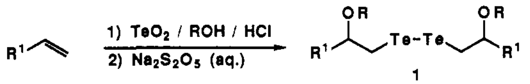
In 1968 a patent procedure described a process for the manufacture of ethylene chlorohydrin from ethylene by using tellurium dioxide, TeO_2, as the catalytic oxidant in aqueous hydrochloric acid (eq 1).[1] Since this transformation seems to be closely related to the well-known

---

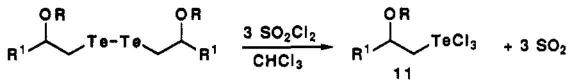
(1) Ger. Off. 1265729, 1968.

$$CH_2{=}CH_2 \xrightarrow[O_2]{TeO_2,\ HCl\ (aq.)} ClCH_2CH_2OH \qquad (1)$$

$$\begin{array}{lcl} C_2H_4 + 1/2\ O_2 + 2\ HOAc & \xrightarrow[HBr]{TeO_2} & AcOCH_2CH_2OAc + H_2O \\ AcOCH_2CH_2OAc + 2\ H_2O & \longrightarrow & HOCH_2CH_2OH + 2\ HOAc \\ \hline C_2H_4 + 1/2\ O_2 + H_2O & \longrightarrow & HOCH_2CH_2OH \end{array} \qquad (2)$$



1 (3)



11 (4)

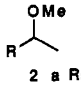
Halcon procedure[2] (tellurium dioxide catalyzed conversion of ethylene to ethylene glycol, eq 2), we thought it should be worthwhile, from a mechanistic point of view, to study the chlorohydrin process in more detail (regiochemistry, stereochemistry, etc.). However, when we replaced ethylene by other olefins in the patent procedure, no oxidation of the double bond occurred. Various cosolvents were therefore added to the reaction medium to increase the solubility of the olefin.

In the following we report the formation of novel alkoxytellurination products by using the system TeO_2/HCl(aq)/ROH for the oxidation of olefins.

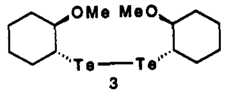
Results

When terminal olefins were heated for 24 h with TeO_2 in refluxing alcoholic aqueous hydrochloric acid and the products, without isolation, were reduced with sodium disulfite, $Na_2S_2O_5$, bis(β-alkoxyalkyl) ditellurides (**1**) were formed according to eq 3. The presence of two or more equivalents of the olefin did not result in the formation of bis adducts (e.g. bis(β-alkoxyalkyl) tellurides) as observed with other electrophilic tellurium(IV) reagents.[3] As seen from Table I, the isolated yields of ditellurides were highly substrate-dependent. The best results were obtained with simple terminal olefins. Even a minor steric hindrance around the double bond reduced the product yield considerably (entries 2–4). A primary hydroxy group, well separated from the terminal olefin by a C9 chain, did not interfere when carried through the reaction sequence (entry 8). However, a similar alcohol acetate was hydrolyzed to give a hydroxy compound in the product ditelluride (entry 12).

The assigned regiochemistry, Markovnikov addition to the double bond, was proven in hydrodetelluration experiments with a few ditellurides, **1**. Thus, treatment of compounds **1f** and **1i** in ethanol with Raney nickel afforded the dialkyl ethers **2a** and **2b** in 48% and 58% yields, respectively.



2 a R=$C_6H_5CH_2$ b R=$C_{10}H_{21}$



3

Generally, nonterminal olefins such as (*E*/*Z*)-2-octene and 2-methyl-1-pentene failed to give any isolable yields of ditellurides. In contrast to the previous examples, elemental tellurium was deposited when these olefins were heated with TeO_2 in methanolic HCl.[4] Cyclohexene, as the exception, afforded the ditelluride **3** in 11% yield when submitted to the usual reaction conditions.

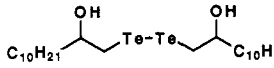
Table I. Preparation of Bis(β-alkoxyalkyl) Ditellurides (1)

1

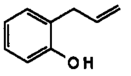
entry	olefin	product[a]	R^1	R	yield, %
1	1-hexene	**1a**	n-C_4H_9	CH_3	58
2	3-methyl-1-pentene	**1b**	sec-C_4H_9	CH_3	22
3	4-methyl-1-pentene	**1c**	i-C_4H_9	CH_3	29
4	styrene	**1d**	C_6H_5	CH_3	18
5	1-octene	**1e**	n-C_6H_{13}	CH_3	72
6	allylbenzene	**1f**	$C_6H_5CH_2$	CH_3	80
7	allylbenzene	**1g**	$C_6H_5CH_2$	C_2H_5	65
8	10-undecen-1-ol	**1h**	HOC_9H_{18}	CH_3	45
9	1-dodecene	**1i**	n-$C_{10}H_{21}$	CH_3	72
10	1-dodecene	**1j**	n-$C_{10}H_{21}$	C_2H_5	55
11	1-dodecene	**1k**	n-$C_{10}H_{21}$	i-C_3H_7	23
12	11-dodecen-1-ol acetate	**1l**	$HOC_{10}H_{20}$	CH_3	41
13	1-hexadecene	**1m**	n-$C_{14}H_{29}$	CH_3	50

[a] All Ditellurides were obtained as diastereomeric mixtures.

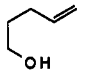
Of the different cosolvents tried, methanol gave the best results (Table I). When a less nucleophilic solvent such as ethanol or isopropyl alcohol was used in the oxidation of 1-dodecene, bis(2-hydroxydodecyl) ditelluride (**4**) was isolated in a 21% or 29% yield, respectively, as well as the bis(β-alkoxyalkyl) ditelluride (Table I, entries 9–11).



4



5

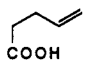


6

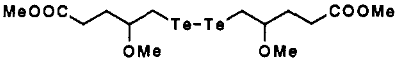
If a suitably positioned nucleophile is present in the olefin to be oxidized, cyclofunctionalization products would result if the nucleophile could compete favorably with the solvent. Such products were isolated when 2-allylphenol (**5**) and 4-penten-1-ol (**6**) were submitted to the usual addition/reduction reaction sequence in methanolic HCl. Compounds **7** and **8** were isolated in 83% and 62% yields, respectively. No products of methoxytellurination were formed with these substrates. When 4-pentene-1-carboxylic acid (**9**) was oxidized in methanolic HCl, the ditelluride **10** was isolated in 71% yield. This material can be formed either by methoxytellurination of the esterified carboxylic acid or by ring opening/esterification of a cyclofunctionalization product (lactone).

7

8



9



10

The bis(β-alkoxyalkyl) ditellurides were isolated by flash chromatography as red viscous oils that could be stored in the freezer for many months without any visible decomposition. By treatment with sulfuryl chloride, SO_2Cl_2, the ditellurides **1** were converted to often[5] highly crystalline

---

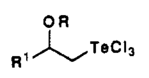
(2) U.S. Patents 3479395, 1969; 3668239, 1972; 3689535, 1972; 3715388, 1973; 3715389, 1973; 3907874, 1975.

(3) Tellurium tetrahalides are known to readily form bis(β-haloalkyl)tellurium dihalides with olefins: Irgolic, K. J. *The Organic Chemistry of Tellurium*; Gordon and Breach: New York, 1974; pp 36, 172.

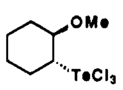
(4) No compounds were isolated from the complex product mixtures formed in these reactions.

(5) All bis(β-alkoxyalkyl) ditellurides prepared afforded (β-alkoxyalkyl)tellurium trichlorides upon treatment with sulfuryl chloride. However, only the crystalline ones reported in Table II were further characterized.

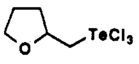
Table II. Preparation of (β-Alkoxyalkyl)tellurium Trichlorides and Related Compounds from Bis(β-alkoxyalkyl) Ditellurides



11



12



13

starting material	product	R^1	R	yield, %	mp, °C
1a	11a	n-C_4H_9	CH_3	79	63–64
1b	11b	*sec*-C_4H_9[a]	CH_3	89	68–70
1c	11c	i-C_4H_9	CH_3	93	90–91
1d	11d	C_6H_5	CH_3	89	112
1f	11e	$C_6H_5CH_2$	CH_3	91	118–119
1g	11f	$C_6H_5CH_2$	C_2H_5	74	68–69
1i	11g	n-$C_{10}H_{21}$	CH_3	91	49
1m	11h	n-$C_{14}H_{29}$	CH_3	89	66–67
3	12			97	126–127
8	13			84	110–112

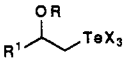
[a] Diastereomeric mixture.

(β-alkoxyalkyl)tellurium trichlorides (eq 4). Table II summarizes yields and melting points of compounds 11 prepared as well as the closely related materials 12 and 13.

By selective proton decoupling we determined the vicinal proton–proton coupling constant of the methine protons of compound 12 ($^3J_{H-H}$ = 10.9 Hz). This indicates a trans arrangement of the oxygen and tellurium elements in the product.

Discussion

Since sodium disulfite is known[6] to reduce various organyltellurium(IV) compounds to the corresponding diorganyl ditellurides, we feel that compounds of structure 14 (X = Cl or an oxygen-containing substituent or a mixture thereof) are intermediates in the reaction sequence leading to ditellurides. As shown in structure 15, these species could form via electrophilic attack on the olefin by a TeX_3^+ reagent, followed by nucleophilic attack of the alcoholic solvent.



14

15

Tellurium dioxide is known to form (via $HTeCl_5$) hydrogen hexachlorotellurate, H_2TeCl_6, when dissolved in 12 M HCl.[7] Similar species were shown to undergo aromatic electrophilic substitution reactions with aromatic amines in methanol to give (aminoaryl)tellurium trihalides.[8]

In one experiment we attempted to isolate the methoxytellurination product from allylbenzene before reduction to a ditelluride. Since the material was extractable into methylene chloride from the reaction mixture, possible tellurate ion forms of compound 14 are not present in substantial amounts.[9] Unfortunately, the isolated glasslike material could not be purified and characterized.[10]

The involvement of small amounts of (β-chloroalkyl)tellurium(IV) species could not be excluded in the ditelluride synthetic sequence. In contrast to (β-alkoxyalkyl)tellurium(IV) compounds, these materials are known to decompose upon treatment with aqueous $Na_2S_2O_5$.[11]

The low yields obtained with terminal olefins bearing branched substituents and the failure, in general, to isolate products from 1,1- and 1,2-disubstituted olefins make the tellurium electrophile unique in its reactivity.[12] This could be a result of severe steric hindrance due to solvation and ligand coordination in the reaction medium.

Nevertheless, our two-step reaction allows the facile synthesis of bis(β-alkoxyalkyl) ditellurides and (β-alkoxyalkyl)tellurium trichlorides not previously available. The ditellurides, since they are readily reduced by $NaBH_4$ to give nucleophilic (β-alkoxyalkyl)tellurolate ions, should prove useful for alkylation reactions. The (β-alkoxyalkyl)tellurium trichlorides could undergo electrophilic addition reactions with olefins and electrophilic aromatic substitution reactions with aromatics.

Alkoxytellurination reactions of olefins are previously known with reagents such as TeO_2/HOAc/LiCl,[13] arenetellurinic anhydrides,[14] and aryltellurium tribromides.[15] However, due to the high reactivity of the tellurium electrophile or the presence of a carbon–tellurium bond already in the electrophile, these reactions always lead to diorganyl tellurides after reductive workup.

In view of the results obtained in this study, the ethylene chlorohydrin process (eq 1) likely involves an electrophilic addition to the olefin (hydroxytellurination). The 1,2 shift of a heteroatom (chlorine) from tellurium to carbon, which is required to arrive at the observed product, has been suggested previously[16] and recently is supported by results from the patent literature.[17]

Experimental Section

Melting points (uncorrected) were determined by using a Büchi 510 melting point apparatus. NMR spectra were obtained at 200 and 400 MHz by using Bruker WP 200 and Bruker AM 400 instruments, respectively. They were recorded in $CDCl_3$ solutions containing Me_4Si as internal standard and are reported in δ units. Elemental analyses were performed by Analytical Laboratories, Engelskirchen, Germany. Sulfuryl chloride was freshly distilled. All olefinic starting materials were commercially available except for 11-dodecen-1-ol acetate which was kindly provided by Chemische Werke Hüls A.G.

Preparation of Bis(β-alkoxyalkyl) Ditellurides. Typical Procedure. Bis(2-methoxy-3-phenylpropyl) Ditelluride (1f). TeO_2 (2.0 g, 12.5 mmol) was dissolved in HCl (10 mL, concentrated) and the yellow solution diluted with MeOH (40 mL). After addition of allylbenzene (1.75 g, 14.8 mmol) the reaction mixture was heated at reflux for 24 h and then allowed to cool to ambient temperature. The yellowish homogeneous solution (containing trace amounts of elemental tellurium) then was poured into a separatory funnel containing $Na_2S_2O_5$ (5 g in 100 mL of H_2O) and CH_2Cl_2 (100 mL). After shaking, the red CH_2Cl_2 phase was separated, dried, and evaporated to give a red oil which was purified by flash chromatography (SiO_2, CH_2Cl_2) to give 2.78 g of compound 1f. ^1H NMR: δ 2.80 (m, 1 H), 2.93 (m, 1 H), 3.28–3.47 (several peaks, 3 H), 3.33 (s, 3 H), 7.16–7.32 (several

---

[6] Reference 3, p 91.

[7] Brill, T. B.; Welsh, W. A. *J. Chem. Soc., Dalton. Trans.* **1973**, 357.

[8] Berry, F. J.; Gupta, A. K.; Khandelwal, B. L.; Raina, K. *J. Organomet. Chem.* **1979**, *172*, 445.

[9] Aryltellurium trihalides are known to dissolve in aqueous HCl to form aryltetrahalotellurate ions, $ArTeX_4^-$: Petragnani, N.; Castellanos, L. T.; Wynne, K. J.; Maxwell, W. *J. Organomet. Chem.* **1973**, *55*, 295.

[10] The material obtained after dilution (H_2O) and extraction (CH_2Cl_2) of the methanolic HCl solution was washed with HCl (10% aqueous), dried, and evaporated to give a solid glasslike material which could not be passed through a column. We were also unable to recrystallize this compound. A ^1H NMR spectrum of the crude product showed very broad lines for all nonaromatic protons. Elemental analysis of the material showed that the product contained a considerable amount of chlorine (19.18%).

[11] Bäckvall, J.-E.; Engman, L. *Tetrahedron Lett.* **1981**, *22*, 1919.

[12] Schmid, G. H.; Garratt, D. G. In *The Chemistry of Double-Bonded Functional Groups*; Patai, S., Ed.; Wiley: London, 1977; Part 2, p 725.

[13] Bergman, J.; Engman, L. *J. Am. Chem. Soc.* **1981**, *103*, 5196.

[14] Hu, N. X.; Aso, Y.; Otsubu, T.; Ogura, F. *Tetrahedron Lett.* **1987**, *28*, 1281.

[15] Uemura, S.; Fukuzawa, S.; Toshimitsu, A. *J. Organomet. Chem.* **1983**, *250*, 203.

[16] Bergman, J.; Engman, L. *J. Organomet. Chem.* **1979**, *181*, 335.

[17] U.S. Patents 4 260 814, 1981; 4 271 090, 1981.

peaks, 5 H). The material was converted to a (β-methoxyalkyl)tellurium trichloride (**11e**) and analyzed as such (vide infra).

The following compounds (^{1}H NMR, analysis [if not analyzed as a (β-alkoxyalkyl)tellurium trichloride]) were obtained as described in the general procedure. For yields of ditellurides 1 prepared see Table I.

1a: δ 0.91 (t, 3 H), 1.26–1.38 (several peaks, 4 H), 1.57 (m, 2 H), 3.21 (m, 1 H), 3.36 (s, 3 H), 3.45 (m, 2 H).

1b: δ 0.85–0.94 (several peaks, 6 H), 1.16 (m, 1 H), 1.47 (m, 1 H), 1.72 (m, 1 H), 3.16 (m, 1 H), 3.32–3.47 (several peaks, 5 H).

1c: δ 0.91 (dd, 6 H), 1.36 (m, 1 H), 1.52 (m, 1 H), 1.73 (m, 1 H), 3.25 (m, 1 H), 3.36 (s, 3 H), 3.46 (m, 2 H).

1d: δ 3.23 (d, 3 H), 3.42 (m, 1 H), 3.59 (m, 1 H), 4.31 (m, 1 H), 7.30–7.35 (several peaks, 5 H).

1e: δ 0.87 (t, 3 H), 1.30 (s, 8 H), 1.56 (m, 2 H), 3.20 (m, 1 H), 3.36 (s, 3 H), 3.45 (m, 2 H). Anal. Calcd for $C_9H_{19}OTe$: C, 39.91; H, 7.07. Found: C, 39.74; H, 6.95.

1g: δ 1.14 (t, 3 H), 2.75–2.95 (several peaks, 2 H), 3.31–3.59 (several peaks, 5 H), 7.16–7.37 (several peaks, 5 H).

1h: δ 1.30 (s, 12 H), 1.57 (m, 4 H), 3.20 (m, 1 H), 3.36 (s, 3 H), 3.45 (m, 2 H), 3.64 (t, 3 H). Anal. Calcd for $C_{12}H_{25}O_2Te$: C, 43.82; H, 7.66. Found: C, 43.67; H, 7.52.

1i: δ 0.88 (t, 3 H), 1.27 (s, 16 H), 1.56 (m, 2 H), 3.20 (m, 1 H), 3.36 (s, 3 H), 3.45 (d, 2 H).

1j: δ 0.88 (t, 3 H), 1.19 (t, 3 H), 1.26 (s, 16 H), 1.55 (m, 2 H), 3.30 (m, 1 H), 3.43–3.57 (several peaks, 4 H). Anal. Calcd for $C_{14}H_{29}OTe$: C, 49.31; H, 8.57. Found: C, 49.22; H, 8.54.

1k: δ 0.88 (t, 3 H), 1.13 (d, 3 H), 1.17 (d, 3 H), 1.26 (s, 16 H), 1.54 (m, 2 H), 3.35–3.41 (several peaks, 3 H), 3.67 (m, 1 H). Anal. Calcd for $C_{15}H_{31}OTe$: C, 50.75; H, 8.80. Found: C, 50.64; H, 8.76.

1l: δ 1.29 (s, 14 H), 1.57 (m, 4 H), 3.20 (m, 1 H), 3.36 (s, 3 H), 3.45 (m, 2 H), 3.64 (t, 3 H). Anal. Calcd for $C_{13}H_{27}O_2Te$: C, 45.53; H, 7.94. Found: C, 45.38; H, 7.80.

1m: δ 0.88 (s, 3 H), 1.26 (s, 24 H), 1.56 (m, 2 H), 3.18 (m, 1 H), 3.36 (s, 3 H), 3.45 (m, 2 H).

3: yield 11%. ^{1}H NMR: δ 1.17–1.33 (several peaks, 3 H), 1.47 (m, 1 H), 1.59 (m, 1 H), 1.84 (m, 1 H), 2.10–2.23 (several peaks, 2 H), 3.08 (m, 1 H), 3.21 (m, 1 H), 3.57 (s, 3 H).

7: yield 83%; mp 59–63 °C. ^{1}H NMR: δ 2.98 (dd, 1 H, J = 7.0 and 15.7 Hz), 3.39 (dd, 1 H, J = 8.9 and 15.7 Hz), 3.53 (m, 1 H), 3.66 (m, 1 H), 4.94 (m, 1 H), 6.75 (d, 1 H, J = 8.0 Hz), 6.84 (t, 1 H), 7.09–7.15 (several peaks, 2 H). Anal. Calcd for C_9H_9OTe: C, 41.45; H, 3.48. Found: C, 41.20; H, 3.48.

8: yield 62%. ^{1}H NMR: δ 1.60 (m, 1 H), 1.90–2.08 (several peaks, 3 H), 3.42 (d, 2 H), 3.77 (m, 1 H), 3.88–4.05 (several peaks, 2 H).

10: yield 71%. ^{1}H NMR: δ 1.87–2.04 (several peaks, 2 H), 2.42 (t, 2 H), 3.27 (m, 1 H), 3.35 (s, 3 H), 3.38–3.47 (several peaks, 2 H), 3.68 (s, 3 H). Anal. Calcd for $C_7H_{13}O_3Te$: C, 30.82; H, 4.80. Found: C, 30.63; H, 4.70.

Bis(2-hydroxydodecyl) ditelluride (4) was isolated in 21% and 29% yields, respectively, during the preparation of compounds **1j** and **1k** (column eluted with CH_2Cl_2/MeOH = 95/5); mp 63–64 °C. ^{1}H NMR: δ 0.88 (t, 3 H), 1.27 (s, 16 H), 1.55 (m, 2 H), 2.15 (s, 1 H), 3.28 (m, 1 H), 3.48 (m, 1 H), 3.68 (m, 1 H). Anal. Calcd for $C_{12}H_{25}OTe$: C, 46.06; H, 8.05. Found: C, 46.18; H, 8.00.

Preparation of (β-Alkoxyalkyl)tellurium trichlorides. Typical Procedure. (2-Methoxy-3-phenylpropyl)tellurium Trichloride (11e). To a stirred solution of ditelluride **1f** (0.50 g, 1.81 mmol) in CCl_4 (2 mL) + hexane (6 mL) was added SO_2Cl_2 (0.37 g, 2.74 mmol) in hexane (2 mL) at 0 °C. After trituration and cooling in a freezer, 0.63 g (91%) of compound **11e** was isolated. ^{1}H NMR: δ 2.94 (dd, 1 H), 3.30 (dd, 1 H), 3.63 (s, 3 H), 4.26 (dd, 1 H), 4.41 (dd, 1 H), 4.58 (m, 1 H), 7.20–7.36 (several peaks, 5 H). ^{13}C NMR: δ 40.74, 59.86, 70.25, 78.71, 127.50, 129.04, 129.32, 134.30. Anal. Calcd for $C_{10}H_{13}Cl_3OTe$: C, 31.35; H, 3.42. Found: C, 31.45; H, 3.40.

The following compounds (NMR, analysis) were prepared as described in the typical procedure. For yields and melting points, see Table II.

11a: ^{1}H NMR δ 0.92 (t, 3 H), 1.28–1.40 (several peaks, 4 H), 1.71–2.00 (several peaks, 2 H), 3.61 (s, 3 H), 4.33–4.45 (several peaks, 3 H). Anal. Calcd for $C_7H_{15}Cl_3OTe$: C, 24.08; H, 4.33. Found: C, 24.22; H, 4.41.

11b: ^{13}C NMR δ 11.61, 11.77, 11.88, 14.73, 22.27, 25.41, 35.52, 36.61, 58.92, 59.65, 66.22, 67.17, 80.96, 82.17. Anal. Calcd for $C_7H_{15}Cl_3OTe$: C, 24.08; H, 4.33. Found: C, 24.01; H, 4.22.

11c: ^{1}H NMR 0.95 (d, 3 H), 1.01 (d, 3 H), 1.65 (m, 2 H), 1.85 (m, 1 H), 3.63 (s, 3 H), 4.38–4.45 (several peaks, 3 H). Anal. Calcd for $C_7H_{15}Cl_3OTe$: C, 24.08; H, 4.33. Found: C, 24.00; H, 4.41.

11d: ^{1}H NMR δ 3.45 (s, 3 H), 4.54 (dd, 1 H), 4.64 (dd, 1 H), 5.20 (m, 1 H), 7.43–7.50 (several peaks, 5 H). Anal. Calcd for $C_9H_{11}Cl_3OTe$: C, 29.28; H, 3.00. Found: C, 29.45; H, 3.05.

11f: ^{1}H NMR δ 1.28 (t, 3 H), 2.95 (dd, 1 H), 3.33 (dd, 1 H), 3.83 (q, 2 H), 4.24 (dd, 1 H), 4.38 (dd, 1 H), 4.65 (m, 1 H), 7.20–7.39 (several peaks, 5 H). Anal. Calcd for $C_{11}H_{15}Cl_3OTe$: C, 33.26; H, 3.81. Found: C, 33.44; H, 3.85.

11g: ^{1}H NMR δ 0.89 (t, 3 H), 1.26–1.35 (several peaks, 16 H), 1.70–1.90 (several peaks, 2 H), 3.63 (s, 3 H), 4.35–4.45 (several peaks, 3 H). Anal. Calcd for $C_{13}H_{27}Cl_3OTe$: C, 36.03; H, 6.28. Found: C, 36.39; H, 6.43.

11h: ^{1}H NMR δ 0.88 (t, 3 H), 1.26 (s, 24 H), 1.65–2.00 (several peaks, 2 H), 3.63 (s, 3 H), 4.35–4.45 (several peaks, 3 H). Anal. Calcd for $C_{17}H_{35}Cl_3OTe$: C, 41.72; H, 7.21. Found: C, 41.59; H, 7.09.

12: ^{1}H NMR δ 1.36–1.43 (several peaks, 3 H), 2.02–2.07 (several peaks, 2 H), 2.21 (m, 1 H), 2.50–2.60 (several peaks, 2 H), 3.51 (s, 3 H), 4.15 (m, 1 H), 4.42 (ddd, 1 H, J = 3.8, 10.9, and 12.5 Hz). Anal. Calcd for $C_7H_{13}Cl_3OTe$: C, 24.22; H, 3.77. Found: C, 24.45; H, 3.85.

13: ^{1}H NMR δ 2.00–2.35 (several peaks, 4 H), 3.90 (m, 1 H), 4.37–4.62 (several peaks, 3 H), 5.14 (m, 1 H). Anal. Calcd for $C_5H_9Cl_3OTe$: C, 18.82; H, 2.84. Found: C, 18.93; H, 2.77.

2-*n*-Dodecyl Methyl Ether (2b). Ditelluride **1i** (0.50 g, 1.53 mmol) was heated at reflux in EtOH (20 mL) with Raney nickel (~1.5 g) until the red color disappeared (~15 min). After filtration, evaporation, and flash chromatography (SiO_2, EtOAc/hexane = 1/99) 0.18 g (58%) of compound **2b**[18] was isolated.

Reduction of compound **1f** similarly afforded 2-methoxy-1-phenylpropane (**2a**)[19] in 48% yield (reaction time ≈ 1.5 h).

Acknowledgment. Financial support by the Swedish Natural Science Research Council is gratefully acknowledged.

Registry No. **1a**, 121444-89-1; **1b**, 121444-90-4; **1c**, 121444-91-5; **1d**, 121444-92-6; **1e**, 121444-93-7; **1f**, 121444-94-8; **1g**, 121444-95-9; **1h**, 121444-96-0; **1i**, 121444-97-1; **1j**, 121444-98-2; **1k**, 121444-99-3; **1l**, 121445-00-9; **1m**, 121445-01-0; **2a**, 10066-31-6; **2b**, 95363-55-6; **3**, 121445-02-1; **4**, 121471-73-6; **5**, 1745-81-9; **6**, 821-09-0; **7**, 121445-03-2; **8**, 121445-04-3; **9**, 591-80-0; **10**, 121445-05-4; **11a**, 121445-06-5; **11b**, 121445-07-6; **11c**, 121445-08-7; **11d**, 121445-09-8; **11e**, 121445-10-1; **11f**, 121445-11-2; **11g**, 121445-12-3; **11h**, 121445-13-4; **12**, 121445-14-5; **13**, 121445-15-6; TeO_2, 7446-07-3; 1-hexene, 592-41-6; 3-methyl-1-pentene, 760-20-3; 4-methyl-1-pentene, 691-37-2; styrene, 100-42-5; 1-octene, 111-66-0; allylbenzene, 300-57-2; 10-undecen-1-ol, 112-43-6; 1-dodecene, 112-41-4; 11-dodecen-1-ol acetate, 35153-10-7; 1-hexadecene, 629-73-2; cyclohexene, 110-83-8.

---

(18) Brown, H. C.; Kurek, J. T.; Rei, M.; Thompson, K. L. *J. Org. Chem.* **1985**, *50*, 1171.

(19) Tiecco, M.; Testaferri, L., Tingoli, M.; Chianelli, D.; Bartoli, D. *Gazz. Chim. Ital.* **1987**, *117*, 423.