Anomalous Addition of Tellurium Tetrachloride to Allylic Esters. Short Synthesis of *trans*-(2*S*,3*S*)-2,3-Epoxybutane

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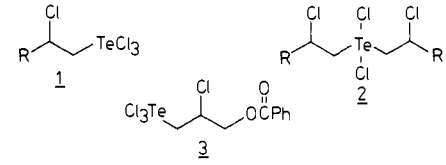
Abstract: The addition of tellurium tetrachloride to various allylic esters, alcohols, ethers, amides, and imino esters was studied. Allylic esters did not produce normal 1,2-chlorotelluration products, but the addition occurred 1,3 and was accompanied by a 1,2-migration of the acyloxy group. The examples include esters of allyl, α-methylallyl, α,α-dimethylallyl, α-ethylallyl, methallyl, and (*E*)-crotyl alcohol, usually with benzoic acid but also with acetic, cinnamic, and crotonic acids. The (β-acyloxy-γ-chloroalkyl)tellurium trichlorides of the 1,3-addition preferred one highly favored conformation in solution, where the acyloxy group was gauche to the $TeCl_3$ group. The 1,3-addition compounds were reduced to β-(acyloxy)-γ-chloroalkyl ditellurides by aqueous Na_2S and hydrodetellurated to chlorohydrin esters with Raney nickel in ethanol. Mechanistically, the elements of Cl and $TeCl_3$ were added to the allylic ester in a 1,3-syn fashion, to allow migration of the acyloxy group on the opposite side of the molecule. α-Substituted allylic esters stereospecifically afforded only the erythro form of the product. Synthetically, with Raney nickel detelluration of the 1,3-addition compounds and ring closure of the chlorohydrin esters, our reaction sequence is equivalent in principle to a direct ring closure of an allylic alcohol to an epoxide. The new strategy was demonstrated in a short synthesis of *trans*-(2*S*,3*S*)-2,3-epoxybutane from (*S*)-α-methylallyl alcohol. The other allylic systems underwent 1,2-addition (ethers), formed zwitterionic compounds (amides), or produced black tarry materials (allylic alcohols) when treated with $TeCl_4$. The 1,3-addition could be extended only to an allyl imino ester, which yielded a (β-amido-γ-chloropropyl)tellurium trichloride.

The relatively undeveloped area of organotellurium chemistry has seen a renaissance in the past decade.[1] This has also resulted in a series of synthetic applications,[2] mainly in the fields of carbon–carbon bond formation[3] and functional group manipulation.[4]

However, few if any of the newly developed methods have yet found wide acceptance and use among organic chemists. This is due in part to the historically bad reputation of organotellurium compounds but also to a lack of uniqueness of the new procedures. In our search for selective transformations using organotellurium reagents, we have recently developed a procedure for olefin inversion.[5,6] Our synthetic sequence was based on a 1,2-syn-chlorotelluration–anti-dechlorotelluration, using tellurium tetrachloride as the chlorotellurating agent. In a continuation of this study, we have now investigated the interaction of tellurium tetrachloride with a series of allylic compounds. Surprisingly, the addition did not produce a normal 1,2-chlorotelluration product with allylic esters but occurred 1,3, with rearrangement of the acyloxy group. The synthetic potential of the new reaction was demonstrated in a conceptually new synthesis of epoxides from allylic alcohols, which culminated in a short synthesis of *trans*-(2*S*,3*S*)-2,3-epoxybutane.

Addition of $TeCl_4$ to Allylic Systems

The addition of $TeCl_4$ to a simple olefin $RCH{=}CH_2$ usually produces a (β-chloroalkyl)tellurium trichloride (**1**)[7-11] or a bis-



1 **2** **3**

(β-chloroalkyl)tellurium chloride (**2**),[9,10,12-14] depending on the relative amounts of the reacting species. The regio- and stereochemistry of the reaction have been studied to some extent.

Thus, only Markovnikov addition was observed for terminal olefins. Concerning the stereochemistry, it has been recently shown that the addition is syn-specific in the presence of a suitable radical inhibitor.[6]

The reaction of allyl benzoate with tellurium tetrachloride proceeded smoothly in chloroform at ambient temperature to give a highly crystalline 1:1 adduct in 94% isolated yield. A proton NMR spectrum of the compound showed a signal for a methine proton at such a low field (5.95 ppm) that the expected structure **3** for this compound seemed unlikely (the methine proton of similar compounds resonates at ~0.5 ppm higher field).[6] Furthermore,

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(2) Ley, S. V. *Annu. Rep. Sect. B* **1980**, *77*, 233.

(3) See, for example: Bergman, J. *Tetrahedron* **1972**, *28*, 3323. Bergman, J.; Carlsson, R.; Sjöberg, B. *Org. Synth.* **1977**, *57*, 18. Bergman, J.; Engman, L. *Tetrahedron* **1980**, *36*, 1275. Bergman, J. *Chem. Scr.* **1975**, *8A*, 116. Bergman, J.; Engman, L. *J. Organomet. Chem.* **1979**, *175*, 233. Uemura, S.; Wakasugi, M.; Okano, M. *Ibid.* **1980**, *194*, 277. Uemura, S.; Fukuzawa, S. *Tetrahedron Lett.* **1982**, *23*, 1181. Uemura, S.; Fukuzawa, S.; Patil, S. R. *J. Organomet. Chem.* **1983**, *243*, 9. Engman, L.; Cava, M. P. *Tetrahedron Lett.* **1981**, *22*, 5251. Clive, D. L. J.; Anderson, P. C.; Moss, N.; Singh, A. *J. Org. Chem.* **1982**, *47*, 1641. Cuthbertson, E.; MacNicol, D. D. *Tetrahedron Lett.*, 1975, 1893.

(4) See, for example: Clive, D. L. J.; Kiel, W. A.; Menchen, S. M.; Wong, C. K. *J. Chem. Soc. Chem. Commun.* **1977**, 657. Ramasamy, K.; Kalyanasundaram, S. K.; Shanmugam, P. *Synthesis* **1978**, 311; **1978**, 545. Uemura, S.; Miyoshi, H.; Okano, M. *Chem. Lett.* **1979**, 1357. Bergman, J.; Engman, L. *Tetrahedron Lett.* **1978**, 3279. Barton, D. H. R.; Ley, S. V.; Meerholz, C. A. *J. Chem. Soc. Chem. Commun.* **1979**, 755. Bergman, J.; Engman, L. *Z.* Naturforsch., *B* **1980**, *35B*, 882. Uemura, S.; Fukuzawa, S. *J. Chem. Soc. Chem. Commun.* **1980**, 1033. Uemura, S.; Fukuzawa, S. *Chem. Lett.* **1980**, 943. Engman, L.; Cava, M. P. *J. Chem. Soc. Chem. Commun.* **1982**, 164, Engman, L.; Cava, M. P. *J. Org. Chem.* **1982**, *47*, 3946. Engman, L. *Tetrahedron Lett.* **1982**, *23*, 3601. Bergman, J.; Engman, L. *J. Org. Chem.* **1982**, *47*, 5191. Osuka, A.; Suzuki, H. *Chem. Lett.* **1983**, 119. Kambe, N.; Kondo, K.; Morita, S.; Murai, S.; Sonoda, N. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 1009. Ley, S. V.; Meerholz, C. A.; Barton, D. H. R. *Tetrahedron Lett.* **1980**, *21*, 1785. Uemura, S.; Fukuzawa, S.; Okano, M. *Ibid.* **1981**, *22*, 5331. Kambe, N.; Kondo, K.; Ishi, H.; Sonoda, N. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 1460. Uemura, S.; Fukuzawa, S.; Wakasugi, M.; Okano, M. *J. Organomet. Chem.* **1981**, *214*, 319. Ley, S. V.; Meerholz, C. A.; Barton, D. H. R. *Tetrahedron, Suppl.* **1981**, *9*, *37*, 213. Clive, D. L. J.; Beaulieu, P. L. *J. Org. Chem.* **1982**, *47*, 1124. Albeck, M.; Tamari, T.; Sprecher, M. *Ibid.* **1983**, *48*, 2276. Uemura, S.; Fukuzawa, S. *J. Am. Chem. Soc.* **1983**, *105*, 2748.

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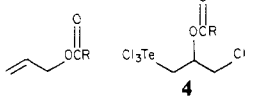
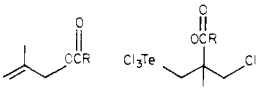
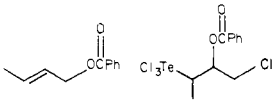
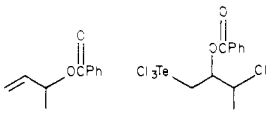
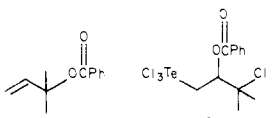
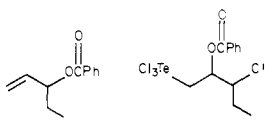
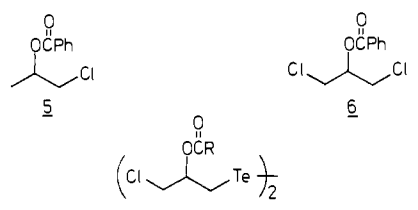
Table I. 1,3-Addition Products of Allylic Esters with $TeCl_4$: Physical, Spectroscopic, and Analytical Data

allylic ester	product: structure	product: no.	% yield[a]	mp, °C[b]	ν(C=O), cm^{-1}	^{1}H NMR data[h]: chemical shift, ppm H_A	H_B	coupling constants, Hz[f] J_{AX}	J_{BX}	analysis: calcd C	calcd H	found C	found H
	4	**4a**, R = C_6H_5	94	165–167	1620	4.08	4.29	*g*	10.4	27.83	2.33	27.98	2.34
		4b, R = 4-Me-C_6H_4	77	165–166	1620	4.06	4.27	1.3	10.5	29.65	2.72	29.62	2.70
		4c, R = 4-Cl-C_6H_4	73	152–153	1620	4.08	4.29	1.3	10.4	25.77	1.95	26.05	1.96
		4d, R = 4-NO_2-C_6H_4	79	167–168	1635	4.14	4.31	1.3	10.3	25.20	1.90	25.24	1.89
		4e, R = CH_3	97	90–91[c]	1630	4.02	4.18	1.5	10.2	16.25	2.18	16.20	2.14
		4f, R = (*E*)-CH=$CHCH_3$	91	100–103[d]	1600	4.00	4.19	1.5	10.4	21.25	2.55	21.35	2.55
		4g, R = (*E*)-CH=CHC_6H_5	74	182–185	1600	4.04	4.25	1.4	10.5	31.49	2.64	31.91	2.70
	10	**10a**, R = C_6H_5	98	135–140 dec	1605	*g*	*g*			29.65	2.72	29.71	2.70
		10b, R = CH_3	76	104–106 dec	1640	*g*	*g*			18.79	2.63	18.87	2.65
	11	**11**	54	177–178 dec	1610	4.30		1.5		29.65	2.72	29.83	2.72
	12	**12**	80	153–156	1620	*g*	*g*	*g*	*g*	29.65	2.72	29.71	2.77
	13	**13**	65	175–180 dec	1630	4.33	4.23	1.6	9.6	31.36	3.07	32.26[e]	3.12
	14	**14**	79	155–157 dec	1620	4.17	4.32	1.4	9.9	31.36	3.07	31.70	3.13

[a] Isolated yields. [b] Unless otherwise indicated, all compounds were recrystallized from acetonitrile. [c] CCl_4. [d] CCl_4/light petroleum, bp 70–80 °C. [e] Despite several recrystallizations, this material never gave an acceptable analysis (small amounts of elemental tellurium always seemed to deposit during the crystallization). [f] The geminal coupling constant, $|J_{AB}|$, was 12.2–12.5 Hz in all cases. [g] Poor resolution or overlapping signals prevented an accurate determination of coupling constants and/or chemical shifts. [h] Diastereotopic protons H_A/H_B are α to tellurium.

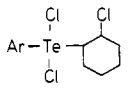
reduction with aqueous sodium sulfide did not regenerate allyl benzoate but produced a red oil, presumably a ditelluride ((β-chloroalkyl)tellurium trichlorides of structure **1** usually undergo an anti elimination on treatment with aqueous Na_2S).[5,6]

It was therefore hypothesized that an acyl migration had occurred during the addition to produce a (β-(acyloxy)-γ-chloropropyl)tellurium trichloride (**4a**) (Table I). Conclusive evidence for structure **4a** was obtained by detelluration with Raney nickel in refluxing ethanol which afforded the chlorohydrin ester **5** in 52% yield as the only product. Treatment of compound **4a** with chlorine in chloroform at ambient temperature, or refluxing acetonitrile containing lithium chloride, afforded 1,3-dichloro-2-propyl benzoate (**6**) in almost quantitative yield.

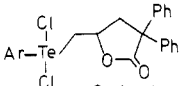


5 6

7 a R = Ph
b R = Me
c R = E-CH=$CHCH_3$
d R = E-CH=CHPh



8 Ar = 1-naphthyl



9 Ar = 1-naphthyl

The observed formation of ditelluride from compound **4a**, on treatment with Na_2S, is now easily explained: Organyltellurium trichlorides in general give ditellurides on treatment with reducing agents like Na_2S. However, if the organic moiety contains a good leaving group in the β-position (e.g., a halogen), an elimination reaction occurs. A benzoyloxy group in the β-position is apparently a sufficiently poor leaving group to allow formation of a ditelluride, **7a**. The same phenomenon was in fact observed also during the reduction of diorganyltellurium dichlorides. These compounds are generally reduced to diorganyl tellurides by Na_2S. However, the unsymmetric compound **8**, containing a 2-chlorocyclohexyl group, was not reduced to a telluride by eliminated cyclohexene on attempted reduction. Compound **9**, containing a β-acyloxy group, could be reduced to the expected telluride.[8]

The 1,3-addition of $TeCl_4$ to allylic esters is a quite general reaction, as can be seen from Table I. The examples include esters of allyl, α-methylallyl, α,α-dimethylallyl, α-ethylallyl, methallyl, and (*E*)-crotyl alcohol, usually with benzoic acid (including 4-Me, 4-Cl, and 4-NO_2) but also with acetic, cinnamic, and crotonic acids. The reaction of $TeCl_4$ with allyl crotonate gave an inseparable mixture of compounds in $CHCl_3$, but fortunately only one isomer separated out in 52% yield if the reaction was carried out in acetonitrile. All other reactions were carried out in dry eth-

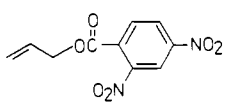
anol-free chloroform at ambient temperature for an extended period of time (usually overnight) or, in a few cases, in refluxing chloroform. The yields were usually good to excellent (Table I), and no compounds of 1,2-addition were formed in isolable amounts. There were also a few allylic esters that produced a black syrupy tar on treatment with $TeCl_4$ under the normal reactions conditions. These include 2-cyclohexenyl acetate, 3-methyl-2-buten-1-yl benzoate and acetate, and cinnamyl benzoate.

The compounds in Table I were converted to ditellurides on treatment with aqueous Na_2S, usually in yields better than 90%. Thus, compounds **4a**, **4e**, **4f**, and **4g**, respectively, yielded the ditellurides **7a–7d** as red viscous oils. The low yield of compound **7b** (14%) seems to indicate that a β-acetoxy group is a sufficiently good leaving group to be eliminated during the reduction process. Compounds **10a** and **11–13**, respectively, afforded the ditellurides **15–18**.

15 16

17 18

A substituent effect was observed for the 1,3-addition of $TeCl_4$ to a series of 4-substituted allyl benzoates (**4a–4d**). Allyl benzoate and 4-methylbenzoate did undergo a reaction at ambient temperature, whereas the 4-chloro- and 4-nitrobenzoates required additional heating at a reflux temperature to go to completion. Allyl (2,4-dinitrophenyl)benzoate (**19**) did not give a 1,3-addition product at all, even on prolonged heating. Allyl trichloroacetate (**20**) did not undergo a reaction with $TeCl_4$; neither did allyl chloride or allyl bromide.



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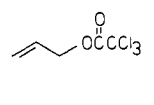

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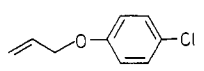

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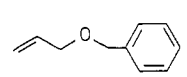

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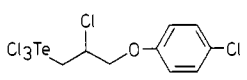

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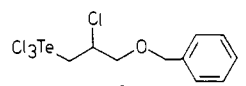

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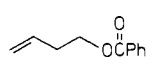

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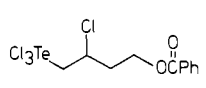

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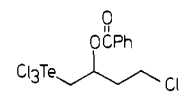


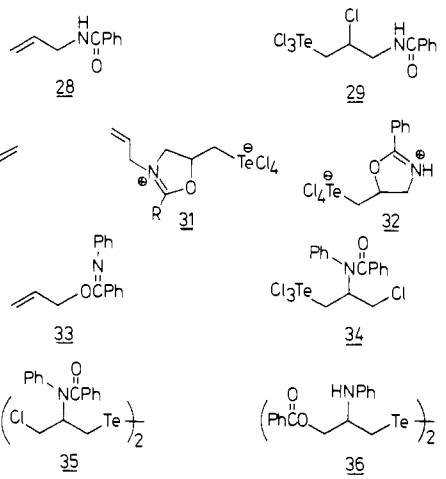
27

An attempt to extend the 1,3-addition reaction to allylic ethers was unsuccessful. Allyl 4-chlorophenyl ether (**21**) and allyl benzyl ether (**22**), respectively, underwent a smooth reaction with $TeCl_4$ in $CHCl_3$ to produce the 1,2-addition compounds **23** and **24**.

The structural assignment was based on the fact that sodium sulfide treatment of compounds **23** and **24** regenerated the respective allylic ether without any formation of a ditelluride.

Our attempt to perform a 1,4-addition to a homoallylic ester also met with failure. 3-Butenyl benzoate (**25**) exclusively underwent 1,2-addition to produce compound **26** in 92% yield instead of its isomer **27**.

The structural assignment of compound **26** was again based on the result from an Na_2S reduction (regeneration of 3-butenyl benzoate in 94% yield). ^1H NMR data also supported this interpretation (methine proton at δ 5.32). When *N*-allylbenzamide (**28**) and $TeCl_4$ were stirred together in CH_3CN, a white high-



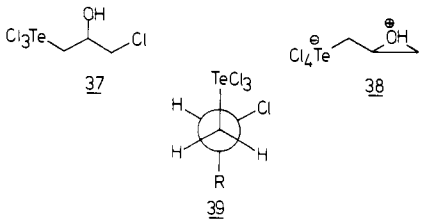
28 29 30 31 32 33 34 35 36

melting (mp >270 °C) solid separated out within a few minutes. The material analyzed well for a 1:1 adduct, and treatment with Na_2S regenerated *N*-allylbenzamide in 92% yield.

These results suggest a 1,2-addition structure **29** for the compound. However, the recent finding by Bergman and co-workers[15] that *N*-acyldiallylamine (**30**) and $TeCl_4$ form zwitterionic 2-oxazolines **31** does suggest an alternative structure. **32**, for our compound. The high melting point of the material and the poor solubility in organic solvents do in fact support this structure.

An example of 1,3-addition with migration of nitrogen was observed during the addition of $TeCl_4$ to the imino ester **33**. The crystalline adduct **34** separated out in 86% yield from a reaction in CH_3CN at ambient temperature. Reduction with aqueous $Na_2S_2O_5$ (the reduction with Na_2S was slow in this case) produced a red solid in 90% yield that did not analyze well for the composition $C_{16}H_{15}ClNOTe$ of structure **35**. An IR absorption at 3330 cm^{-1} indicated an N–H bond in the product. It was therefore concluded that the benzoyl group had migrated during reduction to produce an amino alcohol derivative, **36**. The structure was also in agreement with elemental analysis and confirmed by Raney nickel detelluration (vide infra).

The reaction of $TeCl_4$ with allylic alcohols usually produced black tarry materials. Of the different allylic alcohols tried (the corresponding esters are shown in Table I), only allyl alcohol gave an isolable 1:1 adduct in 69% yield. However, no organic products were characterized when this material was reduced with aqueous Na_2S. The sparingly soluble material readily dissolved in refluxing $CHCl_3$ containing an excess of acetyl and benzoyl chloride, respectively, to give compounds **4e** and **4a** in 79% and 78% yield. These results suggest a 1,3-addition structure, **37**, for the compound. An alternative zwitterionic structure, **38**, might also be compatible with the observed results.[16]



37 38 39

Conformation of the 1,3-Addition Compounds

It was recently shown by means of ^1H nuclear magnetic resonance spectroscopy that a series of (β-chloroalkyl)tellurium trichlorides had one highly preferred conformation, **39**, in solution.[5,6] A weak interaction between the electron-deficient tellurium and the relatively electron-rich β-chloro atom resulted in a gauche orientation of the two groups in the most stable conformation.

(15) Bergman, J.; Sidén, J.; Maartmann-Moe, K. *Tetrahedron*, in press.
(16) It is known that epoxides can be ring-opened by acyl halides to give halohydrin esters. For an example see: Ivin, S. Z. *Zh. Obshch. Khim.* **1958**, *28*, 180.

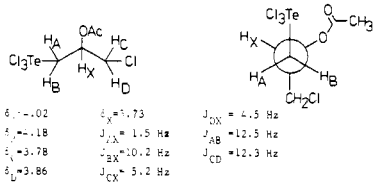


Figure 1.

The 1,3-addition compounds of $TeCl_4$ and allylic esters contain an acyloxy group in the β-position and a chlorine atom in the γ-position. An inspection of the carbonyl frequencies of the different adducts (Table I) shows a dramatic lowering (100–130 cm^{-1}) of the frequency, as compared with a normal ester carbonyl.

This effect is undoubtedly caused by coordination of the carbonyl oxygen to tellurium. This effect has also been observed for several other organotellurium compounds containing an electron-deficient tellurium atom.[17-19] An inspection of the ^1H NMR data of the different 1,3-adducts in Table I gives additional information concerning the conformation of the products. In analyzing the spectra, compound **4e**, the adduct of $TeCl_4$ and allyl acetate, might serve as a typical example (Figure 1). The two pairs of diastereotopic methylene protons, H_A/H_B and H_C/H_D, each appeared as an AB part of an ABX spectrum. The two protons α to tellurium, H_A/H_B, were well separated (4.02 and 4.18 ppm, respectively), and the coupling constants J_{AX} and J_{BX} were quite different (1.5 Hz and 10.2 Hz, respectively). The protons α to chlorine were not so well separated (3.78 and 3.86 ppm, respectively), and the coupling constants J_{CX} and J_{DX} did not differ very much (5.2 and 4.5 Hz, respectively).

The assumption that the $TeCl_3$ group had a more deshielding effect than the chlorine was based on the spectral data of compound **13**. The substitution of H_C and H_D with methyl groups made the high-field methylene signals disappear, while the low-field ones were almost unchanged.

The IR and ^1H NMR data strongly suggest one highly favored conformation of the molecule (Figure 1), where the $TeCl_3$ group is gauche to the acetoxy group and anti to the CH_2Cl group. According to the Karplus equation.[20] there should be a great difference between J_{AX} and J_{BX}, as was also observed. The assigned conformation also explains the greater nonequivalence between H_A/H_B as compared with H_C/H_D. The similar values for J_{CX} and J_{DX} indicate a conformational flexibility of the CH_2Cl group.

In fact. all compounds in Table I conformed very nicely to the above-mentioned analysis, although overlapping signals or poor resolution sometimes prevented a determination of all coupling constants. One of the protons α to tellurium always showed a small vicinal coupling constant (1.3–1.6 Hz), while the other showed a large one (9.6–10.5 Hz) (Table I). It was therefore concluded that all 1,3-adducts preferred a conformation where the $TeCl_3$ and acyloxy groups were gauche to each other.

Mechanism and Stereochemistry of Addition

It was recently shown that the addition of $TeCl_4$ to simple olefins mainly occurred syn, if a competing nonspecific radical addition was inhibited.[6] The 1,3-addition of $TeCl_4$ to allylic esters also seemed to involve addition of the elements of $TeCl_3$ and Cl from the same side of the molecule, to allow migration of the acyloxy group on the opposite side. However, it is not clear whether the reaction is concerted, as shown in Figure 2a, or stepwise ionic. e.g., as shown in Figure 2b.

A radical mechanism is less likely in view of the high specificity of the reactions and the absence of byproducts (the yields in Table I are isolated yields after recrystallization).

The only abnormal case was the addition of $TeCl_4$ to crotyl benzoate in chloroform, which yielded an inseparable mixture of

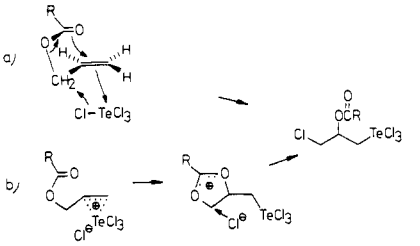


Figure 2.

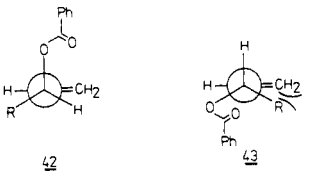
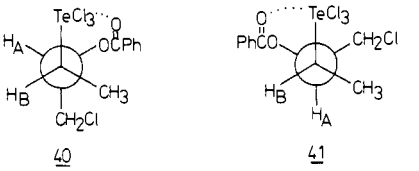


Figure 3.

at least three products. One of these may originate from a reaction with the *Z* isomer of crotyl benzoate (the starting material contained only 80–85% of the *E* isomer).

However, when the solvent was changed to acetonitrile, only one product (assigned structure **11**) separated out. Since the vicinal proton coupling constant J_{AB} was small (1.5 Hz) and the carbonyl absorption low (1610 cm^{-1}), we are left with two possible conformers, **40** and **41**, for the compound (assuming that the $TeCl_3$



and acyloxy groups are gauche to each other and that the elements of Cl and $TeCl_3$ were added from the same side to *E*-crotyl benzoate). This implies that compound **11** has an *erythro* configuration.

The introduction of an α-substituent in the allylic ester creates another type of stereochemical problem (compounds **12** and **14**). The $TeCl_4$ molecule can approach the allyl ester from either of two sides with respect to the plane defined by the three carbons of the allyl group. With esters of allyl alcohol the two approaches are equivalent but with esters of α-alkylallyl alcohols they are not. Figure 3 shows a Newman projection of an α-alkylallyl benzoate, **42**, ready to undergo attack by $TeCl_4$ from *below* the plane. as defined by the allyl group. Conformer **43** shows the same molecule ready to undergo attack from *above* the plane. From inspection of molecular models it is obvious that the conformation **43** is the less favorable one, due to steric repulsion between the alkyl group and one of the terminal methylene hydrogens.

Compounds **12** and **14**, derived from α-methylallyl alcohol and α-ethylallyl alcohol, respectively, were isomerically pure as analyzed by ^1H NMR spectroscopy. Raney nickel detelluration of compound **12** afforded pure *erythro*-2-(benzoyloxy)-3-chlorobutane (**44**) free of the threo isomer as determined by ^1H NMR spectroscopy.[21]

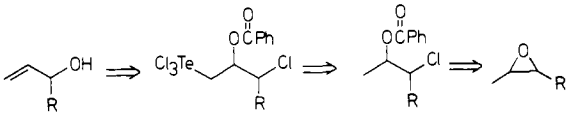
Compounds **12** and **14** have therefore both been assigned the erythro configuration. An inspection of Figure 3 shows that the erythro compounds would be expected if the elements of Cl and $TeCl_3$ were added from below the plane to the favorable conformer **42**.

An analogous addition from above the plane to conformer **43** would produce a threo compound. The difference in activation energy for the two pathways is apparently large enough to allow a completely stereospecific reaction.

(17) Piette, J. L.; Thibaut, P.; Renson, M. *Tetrahedron* **1978**, *34*, 655.
(18) Renson, M.; Piette, J. L. *Specrochim. Acta* **1969**, *20*, 1847.
(19) Engman, L.; Cava, M. P. *J. Org. Chem.* **1981**, *46*, 4194.
(20) Karplus, M. *J. Am. Chem. Soc.* **1963**, *85*, 2870.

(21) Authentic samples of both compounds were available by HClO addition to (*E*)- and (*Z*)-2-butene,[21a] respectively, followed by benzoylation. (a) Huyser, E. S.; Feng, H. C. *J. Org. Chem.* **1971**, *36*, 731.

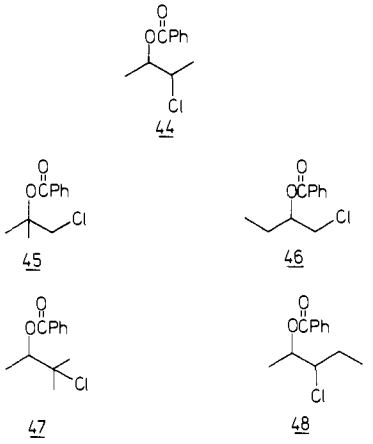
Scheme I



Synthetic Applications

In order to obtain a thorough understanding of the new 1,3-addition reaction of tellurium tetrachloride, much of the work described so far was necessarily concerned with basic organotellurium chemistry and regio- and stereochemical considerations. With the present state of knowledge, it can be noted that the new reaction also has some synthetic potential. If the 1,3-addition is combined with a reductive removal of the $TeCl_3$ group, we have in principle accomplished a ring closure of an allylic alcohol to an epoxide, since the intermediate chlorohydrin ester can be ring-closed after hydrolysis[22] (Scheme I). This roundabout procedure is of course of no practical importance for the preparation of simple epoxides, but it offers certain advantages for more elaborate systems, as will be described in the following.

The different 1,3-addition compounds **4a**, **12**, **10a**, **11**, **13**, and **14** were detellurated by using Raney nickel in refluxing ethanol. The respective chlorohydrin esters, **5**, **44–48**, were usually isolated



in 50–60% yield after 30–60 min. Compound **48** was assigned the erythro configuration, in analogy with the assignment of compound **44** (vide supra).

In the hydrodetelluration reaction, the (β-(acyloxy)-γ-chloroalkyl)tellurium trichlorides are probably first reduced to ditellurides by the Raney nickel. These red compounds were seen during the reduction process and when the reaction was monitored by TLC. The hydrodetelluration step is probably a radical reaction.

Some benzoic acid was always formed during the reduction, which seems to indicate a competing elimination reaction that would account for the modest yield in the hydrodetelluration process. An attempt to remove tellurium with triphenyl tinhydride, according to a method by Clive,[23] was unsuccessful.

The high regio- and stereospecificity observed during the additions of $TeCl_4$ to α-substituted allylic esters led us to investigate the possibility of synthesizing a chiral epoxide from a chiral allylic ester, according to Scheme I. The chirality of the α-carbon would be transferred during the 1,2-migration of the acyloxy group, to produce, after hydrodetelluration, a chiral chlorohydrin ester. α-Methylallyl alcohol appeared to be a good candidate for this kind of reaction, since the absolute configuration was known[24] and the series of reactions to be used had been tried out with the

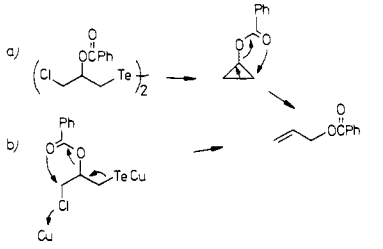
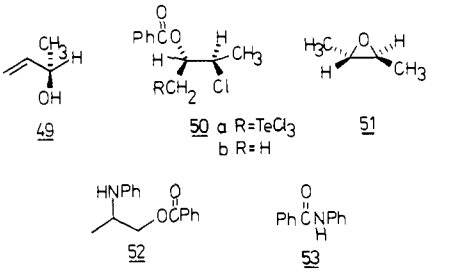


Figure 4.

racemic compound, except for the final ring closure. (*S*)-α-Methylallyl alcohol (**49**) of 92% ee was obtained by the old method

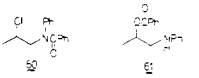


of Kenyon and Snellgrove[25] (resolution of the hydrogen phthalic ester by brucine). Addition of $TeCl_4$ to (*S*)-α-methylallyl benzoate produced (*erythro*-(2*S*,3*R*)-2-(benzoyloxy)-3-chlorobutyl)tellurium trichloride (**50a**), which on hydrodetelluration afforded *erythro*-(2*S*,3*R*)-2-(benzoyloxy)-3-chlorobutane (**50b**).

The final ring closure was performed in 1-pentanol containing potassium amylate, analogously to a literature procedure.[26] The yield in this step was 81% and the enantiomeric excess of the *trans*-(2*S*,3*S*)-2,3-epoxybutane (**51**) was 90% ee, as determined by polarimetry in comparison with an authentic sample. As anticipated, the chirality of the allylic alcohol was transferred, without loss, throughout the reaction sequence.

Attempted hydrodetelluration of compound **34** afforded the new amino alcohol derivative **52** in low yield (20%), in addition to some *N*-phenylbenzamide (**53**). The benzoyl group apparently migrated during the reduction.[27] Compound **52** was obtained in significantly better yield (75%) when the ditelluride **36** was submitted to Raney nickel treatment.

A new kind of detelluration reaction was discovered when the ditellurides **7a**, **7d**, and **15–18** were treated with copper powder in refluxing dioxane. This is usually a standard procedure for the conversion of aromatic ditellurides to tellurides.[28,29] However, our β-(benzoyloxy)-γ-chloroalkyl ditellurides were dechlorotellurated to give allylic benzoates in good yields (58–97%) during these reaction conditions. The benzoyloxy group underwent a 1,2-shift during the reaction to regenerate the same allylic benzoate from which it was synthesized originally (via 1,3-chlorotelluration and sodium sulfide reduction). The following conversions were carried out: **7a** → allyl benzoate, **7d** → allyl cinnamate, **15** →



(22) See, for example: Back, T. G.; Barton, D. H. R.; Rao, B. L. *J. Chem. Soc. Perkin Trans 1* **1977**, 1715. Newman, M. S.; Chen, C. H. *J. Org. Chem.* **1973**, *38*, 1173. Keskinen, R.; Nikkilä, A.; Pihlaja, K. *J. Chem. Soc., Perkin Trans 2* **1977**, 343.

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

(24) Young, W. G.; Caserio, F. F., Jr. *J. Org. Chem.* **1961**, *26*, 245.

(25) Kenyon, J.; Snellgrove, D. R. *J. Chem. Soc.* **1925**, 1169.

(26) Byström, S.; Högberg, H.-E.; Norin, T. *Tetrahedron* **1981**, *37*, 2249.

(27) (a) For reference purposes, we tried to synthesize compound **60** by ring opening of propylene oxide with aniline, followed by Schotten–Baumann benzoylation and treatment with thionyl chloride.[27b] However, we were only able to isolate a small amount of a compound assigned structure **61** (IR 1700, 3390 cm^{-1}; ^1H NMR δ 1.44 (d, 3 H), 3.35–3.46 (several peaks, 2 H), 5.38 (m, 1 H), 6.65–6.76 (several peaks, 3 H), 7.18 (t, 2 H), 7.44 (t, 2 H), 7.57 (m, 1 H), 8.00–8.06 (several peaks, 2 H) where the benzoyl group had migrated. Our material had the same melting point (54 °C) as the one reported for compound **60**. (b) Fourneau, J.-P. *Bull. Soc. Chim. Fr.* **1944**, *11*, 141.

(28) Sadekov, I. D.; Bushkov, A. Y.; Minkin, V. I. *Zh. Obshch. Khim.* **1973**, *43*, 815.

(29) Engman, L. *J. Org. Chem.* **1983**, *48*, 2920.

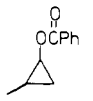
methylallyl benzoate, **16** → crotyl benzoate, **17** → α-methylallyl benzoate, and **18** → α,α-dimethylallyl benzoate. The ditelluride **36** did not change when heated in dioxane with copper powder. A possible mechanism for the dechlorotelluration would involve formation of cyclopropyl benzoate which could rearrange to an allylic benzoate (Figure 4a shows the example **7a** → allyl benzoate).

However, this mechanism is incompatible with the observation that the ditellurides always seem to "remember" from which allylic ester they were once synthesized. Compounds **16** and **17** gave different allylic esters, but according to the cyclopropane mechanism, they should have a common intermediate, **54**.

We therefore hypothesize that the mechanism might involve a copper(I) tellurolate that would undergo 1,3-elimination as shown in Figure 4b.

Discussion

The chemical literature shows relatively few rearrangements of the kind observed during the 1,3-addition of $TeCl_4$ to allylic esters. However, bromine addition to allyl benzoate produced a mixture of the two isomers **55** and **56**.[30] Treatment of allyl



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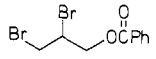

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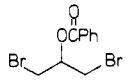

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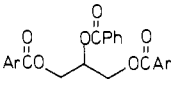

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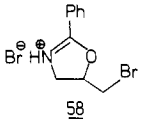

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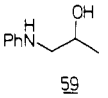

59

benzoate with the complex $(ArCOO)_2AgI$ similarly caused migration of the benzoyloxy group to give the symmetrical triester **57** of glycerol.[31]

Winstein has studied neighboring group participation in the process of addition of an electrophilic reagent to a carbon–carbon double bond.[32] Allyl alcohol and allyl acetate gave normal 1,2-addition compounds with halogens, whereas α,α-dimethylallyl alcohol and *N*-allylbenzamide (**28**) afforded cyclic compounds due to participation of the neighboring group (e.g., compound **28** gave the oxazolium salt **58** on treatment with Br_2).

The high regio- and stereospecificity of the tellurium tetrachloride 1.3-addition makes it a rather outstanding reaction. All attempts to find another similar reagent in the calcogen series met with failure. Thus, phenylselenyl chloride and selenium tetrachloride underwent a smooth reaction with allyl benzoate, but only to produce a mixture of unrearranged adducts. Tellurium tetrabromide was not reactive enough to add to allyl benzoate.

The different regiochemistry observed for allylic esters as compared with allylic ethers in the $TeCl_4$ addition is noteworthy and can be rationalized in the following way: It is known that a chlorine[6] or an ethoxy[11] group offers a certain degree of stabilization when situated β to an electron-deficient $TeCl_3$ moiety, although the interaction has to occur in a four-membered ring. If an allylic ether was to undergo a 1,3-addition instead of a 1,2-addition, this would give rise to a 1,4 tellurium–oxygen interaction plus a 1,5 tellurium–chloride interaction as compared with a 1,4 tellurium–chlorine interaction in addition to a 1,5 tellurium–oxygen interaction. In energy terms the difference between the two arrangements is probably not very large. On the other hand, if an allylic ester was to undergo a 1,2-addition instead of a 1,3-addition, this would give rise to a 1,4 tellurium–chlorine interaction plus a 1.7 carbonyl oxygen–tellurium interaction as compared with a 1,5 tellurium–chlorine and a 1,6 tellurium–carbonyl oxygen interaction. Assuming that the tellurium–carboxyl oxygen interaction is by far the most important, we can understand, in a qualitative way, why the acyloxy group migrates to a more favorable position with respect to coordination (six-membered ring instead of seven-membered).

The complete regio- and stereospecificity of the 1,3-addition of $TeCl_4$ to allylic esters was the basis for a conceptually new, short synthesis of *trans*-(2*S*,3*S*)-2,3-epoxybutane (**51**). This compound is traditionally prepared from (2*R*,3*R*)-tartaric acid via a high-yield multistep procedure (at least eight steps).[26,33,34] Although our synthesis involves only half as many steps, it is not very practical due to the inavailability of the chiral allylic alcohol **49**, from which it starts. However, this situation might change very soon if the field of asymmetric reduction continues to develop. Chiral allylic alcohols are available by asymmetric 1,2-reductions of α,β-unsaturated ketones[35] (e.g., compound **49** from methyl vinyl ketone), but the optical yields in these processes have to be improved if they are to be useful.

The $TeCl_4$ 1,3-addition might find some use today for the synthesis of chlorohydrin esters or epoxides of a certain configuration. For example, the *erythro*-chlorohydrin ester **48** would not be readily available by conventional techniques. However, the stereospecificity of the $TeCl_4$ addition allows the synthesis of erythro compounds only.

A 1,2-migration of an amino group during the 1,3-addition of $TeCl_4$ was demonstrated in only one example (compound **34**). In combination with hydrodetelluration (and migration of the benzoyl group), the new amino alcohol derivative **52** was obtained in good yield. This simple molecule has an interesting orientation of the functional groups, since the amino group is secondary. A ring opening of propylene oxide by aniline would give, almost exclusively, the isomer **59** with a secondary hydroxy and primary phenylamino group.

The synthesis of these "abnormal"[36] amino alcohol derivatives, using organotellurium methodology, is presently being investigated in our laboratories.

Experimental Section

Melting points were uncorrected. NMR spectra were obtained with a Bruker WP 200 instrument at 200 MHz. They are recorded in $CDCl_3$ solutions (unless otherwise stated) containing Me_4Si as internal standard and are reported in δ units. IR spectra were recorded with a Perkin-Elmer 257 instrument (in KBr unless otherwise stated). $TeCl_4$ was sublimed before use and finely crushed with a glass rod. The chloroform was washed repeatedly with water to remove any trace of EtOH and dried over $CaCl_2$. The acetonitrile was predried over $CaCl_2$, distilled, and stored over 4-Å molecular sieves. All allylic alcohols used were commercially available, except for (*S*)-α-methylallyl alcohol.[25,37] The different allylic benzoates were prepared from equivalent amounts of an allyl alcohol, pyridine, and a suitable benzoyl chloride in dry ether, in analogy with literature methods.[38,39] Allylic acetates were prepared in refluxing acetic anhydride containing some pyridine. Allyl crotonate,[40]

(30) Nayler, J. H. *J. Chem. Soc.* **1959**, *189*.
(31) Tisserand, M. *C. R. Hebd. Acad. Sci., Ser. C*: **1966**, *263*, 1550; **1967**, *264*, 531; **1967**, *265*, 392.
(32) (a) Winstein, S.; Goodman, L. *J. Am. Chem. Soc.* **1954**, *76*, 4368. (b) *Ibid.* **1954**, *76*, 4373. (c) *Ibid.* **1957**, *79*, 4788.
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allyl cinnamate,[41] allyl trichloroacetate,[42] allyl 4-chlorophenyl ether,[43] allylbenzyl ether,[44] *N*-allylbenzamide,[32c] allyl (*N*-phenylimino)benzoate,[45] and copper powder[46] were prepared as described in the literature.

Preparation of 1,3-Adducts of $TeCl_4$ with Allylic Esters. For yields, melting points, IR and selected ^1H NMR data (methylene protons α to tellurium) see Table I.

Typical Procedure: (2-Acetoxy-3-chloropropyl)tellurium Trichloride (4e). $TeCl_4$ (2.55 g, 9.5 mmol) and allyl acetate (0.96 g, 9.6 mmol) were stirred overnight in $CHCl_3$ (20 mL) at ambient temperature. The reaction mixture was then heated to reflux and filtered from some insoluble material. After evaporation and crystallization from CCl_4, 3.40 g of compound **4e** was obtained. ^1H NMR: δ 2.36 (s, 3 H), 3.78 (dd, 1 H, J = 5.2 Hz and J = 12.3 Hz), 3.86 (dd, 1 H, J = 4.5 Hz and J = 12.3 Hz), 5.73 (m, 1 H).

The following compounds were analogously prepared.

4a: ^1H NMR δ 3.88–4.02 (several peaks, 2 H), 5.95 (m, 1 H), 7.54 (t, 2 H), 7.75 (t, 1 H), 8.13 (d, 2 H).

4b: ^1H NMR δ 2.47 (s, 3 H), 3.86–4.02 (several peaks, 2 H), 5.93 (m, 1 H), 7.33 (d, 2 H), 8.01 (d, 2 H).

10a: ^1H NMR δ 1.99 (s, 3 H), 3.86 (d, 1 H, J = 12.2 Hz), 4.28–4.46 (several peaks, 3 H), 7.53 (t, 2 H), 7.73 (t, 1 H), 8.10 (dd, 2 H).

10b: ^1H NMR δ 1.83 (s, 3 H), 2.33 (s, 3 H), 3.73 (d, 1 H, J = 12.3 Hz), 4.26–4.32 (several peaks, 3 H).

12: ^1H NMR δ 1.74 (d, 3 H, J = 6.9 Hz), 4.13–4.31 (several peaks, 2 H), 4.46 (dq, 1 H, J = 3.8 and 6.9 Hz), 5.83 (m, 1 H), 7.55 (t, 2 H), 7.75 (t, 1 H), 8.11 (dd, 2 H).

14: ^1H NMR δ 1.20 (t, 3 H), 1.95–2.05 (several peaks, 2 H), 4.28 (m, 1 H), 5.90 (m, 1 H), 7.54 (t, 2 H), 7.74 (t, 1 H), 8.11 (dd, 2 H).

After being stirred overnight according to the general procedure, the reaction mixture was heated to reflux for some time before it was filtered and evaporated. The reflux period is indicated for each of the following compounds.

4c: reflux 1 h; ^1H NMR δ 3.87–4.03 (several peaks, 2 H), 5.95 (m, 1 H), 7.52 (d, 2 H), 8.05 (d, 2 H).

4d: reflux 2 h; ^1H NMR δ 3.91–4.08 (several peaks, 2 H), 6.02 (m, 1 H), 8.27–8.41 (several peaks, 4 H).

4f: reflux 0.5 h; ^1H NMR δ 2.04 (dd, 3 H), 3.80 (dd, 1 H, J = 5.3 and 12.2 Hz), 3.87 (dd, 1 H, J = 4.3 and 12.2 Hz), 5.75 (m, 1 H), 6.05 (d, 1 H), 7.44 (m, 1 H).

4g: reflux 0.5 h; ^1H NMR δ 3.85 (dd, 1 H, J = 5.3 and 12.3 Hz), 3.93 (dd, 1 H, J = 4.3 and 12.3 Hz), 5.85 (m, 1 H), 6.60 (d, 1 H), 7.44–7.51 (several peaks, 3 H), 7.60–7.65 (several peaks, 2 H), 7.99 (d, 1 H).

Compound 11. $TeCl_4$ and crotyl benzoate wer stirred in CH_3CN (15 mL) for 3 h at 0 °C and then overnight at ambient temperature. Filtration afforded compound **11** as a white powder: ^1H NMR δ 2.08 (d, 3 H, J = 7.3 Hz), 3.83 (dd, 1 H, J = 5.2 and 11.8 Hz), 4.02 (dd, 1 H, J = 8.3 and 11.8 Hz), 6.04 (m, 1 H), 7.54 (t, 2 H), 7.74 (m, 1 H), 8.08–8.13 (several peaks, 2 H).

Compound 13. $TeCl_4$ and α,α-dimethylallyl benzoate were heated to reflux for 2.5 h. Filtration and evaporation afforded compound **13**: ^1H NMR δ 1.81 (s, 3 H), 1.83 (s, 3 H), 5.68 (m, 1 H), 7.48–7.59 (several peaks, 2 H), 7.75 (m, 1 H), 8.11 (dd, 2 H).

2-(Benzoyloxy)-1,3-dichloropropane (6). Compound **4a** (0.50 g, 1.16 mmol) was heated to reflux in CH_3CN (15 mL) containing LiCl (0.38 g, 8.9 mmol). A slow stream of Cl_2 was allowed to bubble through the solution for 1.5 h. Evaporation of the solvent and filtration through silica (CH_2Cl_2) afforded 0.26 g (96%) of compound **6**, compared with an authentic sample. Compound **6** was also obtained when a solution of compound **4a** in $CHCl_3$ was saturated with Cl_2 and kept for a few days at ambient temperature. However, the product was less pure, probably as a result of overchlorination.

Preparation of Ditellurides. Typical Procedure: Bis(2-(benzoyloxy)-3-chloropropyl)ditelluride (7a). Compound **4a** (0.80 g, 1.85 mmol) was shaken in CH_2Cl_2 (40 mL) with $Na_2S{\cdot}9H_2O$ (20% aqueous, 30 mL) in a separatory funnel until all material had dissolved. Separation, drying, and evaporation yielded 0.48 g (80%) of compound **7a** as a red oil, after filtration through a short silica column (CH_2Cl_2): IR (neat 1725 cm^{-1}; ^{13}C NMR δ 5.39 (t) and 5.62 (t) (carbon α to Te, two diastereomers), 45.76 (t), 74.73 (d), 128.39, 129.51, 129.78, 133.27, 165.38; ^1H NMR δ 3.63–3.68 (several peaks, 2 H), 3.87–3.91 (several peaks, 2 H), 5.37 (m, 1 H), 7.44 (t, 2 H), 7.55 (t, 1 H), 8.05 (d, 2 H). Anal. Calcd for $C_{10}H_{10}ClO_2Te$: C, 36.93; H, 3.10. Found: C, 37.47; H, 3.22.

The following compounds were prepared in a similar way.

7b: oil, yield 14%; ^1H NMR δ 2.04 (s, 3 H), 3.37–3.49 (several peaks, 2 H), 3.69–3.72 (several peaks, 2 H), 5.07 (m, 1 H).

7c: oil, yield 50%; ^1H NMR δ 1.90 (dd, 3 H), 3.51–3.58 (several peaks, 2 H), 3.78–3.81 (several peaks, 2 H), 5.13 (m, 1 H), 5.86 (dd, 1 H), 7.04 (m, 1 H).

7d: oil, yield 95%; ^1H NMR δ 3.58–3.64 (several peaks, 2 H), 3.84–3.86 (several peaks, 2 H), 5.29 (m, 1 H), 6.44 (dd, 1 H), 7.37–7.41 (several peaks, 3 H), 7.51–7.55 (several peaks, 2 H), 7.73 (dd, 1 H).

15: oil, yield 92%; ^1H NMR δ 1.76 (s, 3 H), 3.88–4.22 (several peaks, 4 H), 7.43 (t, 2 H), 7.56 (m, 1 H), 8.00 (dd, 2 H).

16: oil, yield 92%; ^1H NMR δ 1.55, 1.59 (two doublets, 3 H, due to diastereomers), 3.64–3.69 (several peaks, 2 H), 4.37 (m, 1 H), 5.28 (m, 1 H), 7.46 (t, 3 H), 7.59 (t, 1 H), 8.05 (d, 2 H).

17: oil, yield 80%; ^1H NMR δ 1.72 and 1.74 (two doublets, 3 H, due to diastereomers), 3.84–4.04 (several peaks, 3 H), 5.36 (m, 1 H), 7.47 (t, 2 H), 7.60 (t, 1 H), 8.07 (d, 2 H).

18: mp 103–05 °C (light petroleum, bp 70–80 °C); yield 96%. Anal. Calcd for $C_{12}H_{14}ClO_2Te$: C, 40.80; H, 3.99. Found: C, 40.71; H, 3.98. ^1H NMR: δ 1.61, 1.64, 1.65, 1.67 (four peaks, 6 H, due to diastereomers), 3.58 (m, 1 H), 3.84 (m, 1 H), 5.36, 5.50 (two doublet of doublets, 1 H), 7.40–7.50 (several peaks, 2 H), 7.50–7.60 (m, 1 H), 8.04–8.10 (several peaks, 2 H).

(2-Chloro-3-(4-chlorophenoxy)propyl)tellurium Trichloride (23). $TeCl_4$ (1.60 g, 5.9 mmol) and 4-chlorophenyl allyl ether (1.0 g, 6.0 mmol) were stirred overnight in $CHCl_3$ (40 mL) and heated to reflux for 3 h. Filtration from a small amount of insoluble material and precipitation by addition of light petroleum (bp 40–60 °C) yielded 2.46 g (95%) of compound **23**, mp 122–24 °C (CCl_4): ^1H NMR δ 4.33–4.54 (several peaks, 2 H), 4.91 (m, 1 H), 5.03 (m, 1 H), 5.46 (dd, 1 H, J = 5.7 8.2 Hz), 6.98 (d, 2 H), 7.33 (d, 2 H). Anal. Calcd for $C_9H_9Cl_5OTe$: C, 24.68; H, 2.07. Found: C, 24.56; H, 2.08.

When compound **23** was reduced with aqueous Na_2S, according to the general procedure for ditelluride formation, 4-chlorophenyl allyl ether was obtained in quantitative yield.

(2-Chloro-3-(benzyloxy)propyl)tellurium Trichloride (24). $TeCl_4$ was allowed to react with allyl benzyl ether following the preparation of compound **23**. The resulting oil (free of starting material as determined by ^1H NMR) regenerated allyl benzyl ether (82% yield) on treatment with aqueous Na_2S.

(2-Chloro-4-(benzoyloxy)butyl)tellurium Trichloride (26). $TeCl_4$ (1.03 g, 3.8 mmol) and 3-butenyl benzoate (0.69 g, 3.9 mmol) were rapidly heated to reflux in $CHCl_3$ (15 mL) and stirred at ambient temperature for 1 h. Addition of light petroleum (bp 40–60 °C) caused precipitation of 1.56 g (92%) of a white powder, mp 115–18 °C. Since all attempts to recrystallize the material were unsuccessful, the crude product was analyzed: IR 1660 cm^{-1}; ^1H NMR δ 2.38–2.46 (several peaks, 2 H), 4.43–4.79 (several peaks, 4 H), 5.32 (m, 1 H), 7.47 (t, 2 H), 7.61 (m, 1 H), 8.05 (dd, 2 H). Anal. Calcd for $C_{11}H_{12}Cl_4O_2Te$: C, 29.65; H, 2.72. Found: C, 29.00; H, 2.68.

***N*-Allylbenzamide and $TeCl_4$.** $TeCl_4$ (0.81 g, 3.0 mmol) and *N*-allylbenzamide (0.50 g, 3.1 mmol) were stirred in CH_3CN (5 mL) for 1 h at ambient temperature. A high-melting solid (1.21 g, 94%, mp >270 °C) was then filtered off: IR 1650 cm^{-1}. Anal. Calcd for $C_{10}H_{11}Cl_4NOTe$: C, 27.89; H, 2.57. Found: C, 28.01; H, 2.69. A structure **32** was assigned to this compound, although this could not be shown without doubt. Reduction with Na_2S regenerated *N*-allylbenzamide in 91% yield.

(*N*-Phenyl-2-benzamido-3-chloropropyl)tellurium Trichloride (34). $TeCl_4$ (0.68 g, 2.5 mmol) and allyl *N*-phenyliminobenzoate (0.60 g, 2.5 mmol) were stirred overnight in CH_3CN (5 mL) at ambient temperature. Filtration afforded 1.10 g (86%) of compound **34**, mp 150–55 °C dec (CH_3CN): IR 1600 cm^{-1}; ^1H NMR (Me_2SO, d, 6) δ 3.66 (dd, 1 H, J = 3.2 and 11.7 Hz), 3.78 (dd, 1 H, J = 9.0 and 11.7 Hz), 4.56 (d, 2 H), 4.66 (m, 1 H), 6.65 (t, 1 H), 6.82 (d, 2 H), 7.11 (t, 2 H), 7.43 (t, 2 H), 7.59 (t, 1 H), 7.92 (dd, 2 H). Anal. Calcd for $C_{16}H_{15}Cl_4NOTe$: C, 37.93; H, 2.98. Found: C, 38.38; H, 3.11.

Bis(2-phenylamino-3-(benzoyloxy)propyl) Ditelluride (36). Compound **34** (3.5 g, 6.9 mmol) was shaken with $Na_2S_2O_5$ (10% aqueous, 100 mL) and methylene chloride (200 mL) until all material had dissolved. The red organic phase yielded 2.37 g (90%) of compound **36** after drying, evaporation, and filtration through a short silica column (CH_2Cl_2): mp 104–06 °C (light petroleum, bp 70–80 °C); IR 1700, 3330 cm^{-1}. ^1H NMR δ 3.45–3.50 (several peaks, 2 H), 3.80–4.00 (several peaks, 2 H), 4.30 (m, 1 H), 4.55 (m, 1 H), 6.68–6.77 (several peaks, 3 H), 7.17 (t, 2 H), 7.43 (t, 2 H), 7.57 (t, 1 H), 7.99 (d, 2 H). Anal. Calcd for $C_{16}H_{16}NO_2Te$: C, 50.32; H, 4.22. Found: C, 50.17; H, 4.35.

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Allyl Alcohol and $TeCl_4$. $TeCl_4$ (1.04 g, 3.86 mmol) was heated in $CHCl_3$ (15 mL) with allyl alcohol (0.25 g, 4.31 mmol) until all material had dissolved (5–10 min at reflux). The colorless solution was then allowed to cool. After 2 days at ambient temperature 0.87 g (69%) of white crystals was filtered off: mp 140–50 °C (when dropped on a Koeffler bench); IR 3400 (broad) cm^{-1}; ^1H NMR ($CDCl_3/CD_3CN$) δ 3.88 (t, 1 H, J = 11.0 Hz), 4.00 (t, 1 H, J = 9.8 Hz), 4.38 (dd, 1 H, J = 5.6 and 10.7 Hz), 4.56 (dd, 1 H, J = 5.0 and 9.5 Hz), 4.75 (m, 1 H). Anal. Calcd for $C_3H_6Cl_4OTe$: C, 11.00; H, 1.85. Found; C, 11.10; H, 1.84.

The material (0.10 g, 0.31 mmol) dissolved in refluxing $CHCl_3$ (5 mL) containing acetyl chloride (0.05 g, 0.64 mmol) to give 0.09 g (79%) of compound **4e** after evaporation and recrystallization.

Benzoylation with benzoyl chloride similarly afforded compound **4a** in 78% yield.

Raney Nickel Detelluration of 1,3-Adducts of $TeCl_4$. Typical Procedure: 2-(Benzoyloxy)chloropropane (5). Compound **4a** (0.50 g, 1.16 mmol) and Raney nickel (~1.5 g) were heated to reflux in EtOH (30 mL) for ~1 h. The reaction mixture was monitored by TLC and not disrupted until the ditelluride **7a** (which was formed during the reduction) had disappeared. After filtration and evaporation, the organic products were extracted into ethyl ether and washed with aqueous sodium bicarbonate (some benzoic acid, mp 122 °C, was obtained from the aqueous phase on acidification). Compound **5** (0.12 g, 52%) was obtained from the organic phase and compared with an authentic sample prepared by benzoylation of 1-chloro-2-propanol: ^1H NMR δ 1.47 (d, 3 H), 3.71 (d, 2 H), 5.36 (m, 1 H), 7.45 (t, 2 H), 7.58 (m, 1 H), 8.06 (dd, 2 H).

The following compounds were similarly prepared.

***erythro*-44**: yield 58%; ^1H NMR δ 1.43 (d, 3 H, J = 6.4 Hz), 1.57 (d, 3 H, J = 6.8 Hz), 4.25 (dq, 1 H, J = 4.5 and 6.8 Hz), 5.24 (dq, 1 H, J = 4.5 and 6.8 Hz), 7.45 (t, 2 H), 7.58 (t, 1 H), 8.07 (dd, 2 H). An authentic sample of this compound, as well as the *threo* isomer, was prepared according to literature methods.[21a]

45: yield 26%; ^1H NMR δ 1.68 (s, 6 H), 3.94 (s, 2 H), 7.43 (t, 2 H), 7.56 (m, 1 H), 8.01 (dd, 2 H).

46: yield 50%; ^1H NMR δ 1.01 (t, 3 H), 1.87 (m, 2 H), 3.73–3.76 (several peaks, 2 H), 5.24 (m, 1 H), 7.46 (t, 2 H), 7.59 (m, 1 H), 8.08 (dd, 2 H).

47: yield 78%; ^1H NMR δ 1.45 (d, 3 H), 1.64 (s, 6 H), 5.23 (q, 1 H), 7.41–7.49 (several peaks, 2 H), 7.56 (m, 1 H), 8.05–8.10 (several peaks, 2 H).

***erythro*-48**: yield 61%; ^1H NMR δ 1.10 (t, 3 H), 1.44 (d, 3 H), 1.70–1.97 (several peaks, 2 H), 4.06 (m, 1 H), 5.29 (m, 1 H; the coupling to the CHCl-proton was determined by selective proton decoupling; J = 4.6 Hz), 7.45 (t, 2 H), 7.58 (m, 1 H), 8.06 (dd, 2 H).

2-(Phenylamino)-1-(benzoyloxy)propane (52). Ditelluride **36** was submitted to Raney nickel hydrodetelluration as described above. Compound **52** was isolated in 75% yield, mp 71–72 °C (light petroleum, bp 60–70 °C): IR 1700, 3380 cm^{-1}; ^1H NMR δ 1.34 (d, 3 H), 3.68 (broad s, 1 H), 3.94 (m, 1 H), 4.22 (dd, 1 H, J = 5.6 and 11.0 Hz), 4.48 (dd, 1 H, J = 5.2 and 11.0 Hz), 6.70–6.76 (several peaks, 3 H), 7.19 (t, 2 H), 7.44 (t, 2 H), 7.54 (m, 1 H), 8.00–8.05 (several peaks, 2 H). Anal. Calcd for $C_{16}H_{17}NO_2$: C, 75.27; H, 6.71. Found: C, 74.94; H, 6.71.

Attempted reduction of compound **34** afforded a mixture of compound **52** (20%) and *N*-phenylbenzamide (**53**) (26% yield), mp 163 °C (lit. 163 °C).[47]

***trans*-(2*S*,3*S*)-2,3-Epoxybutane (51).** The enantiomeric purity of the (*S*)-α-methylallyl alcohol (**49**) was conveniently determined by preparation of an ester with (+)-α-methoxy-α-(trifluoromethyl)phenylacetic acid (MTPA ester).[48] The α-methyl groups of the esters resonated at 1.36 (*R*) and 1.43 (*S*) ppm, respectively. The enantiomeric purity of the α-methylallyl alcohol was 92% ee, as determined by integration. Benzoylation using benzoyl chloride/pyridine/ethyl ether afforded (*S*)-α-methylallyl benzoate, $[\alpha]^{20}_D$ +48.03° (EtOH). $TeCl_4$ addition and hydrodetelluration were performed as described for the racemate. The optical rotation were determined as follows.

(*erythro*-(2*S*,3*R*)-2-(Benzoyloxy)-3-chlorobutyl)tellurium trichloride (**50a**): $[\alpha]^{20}_D$ +14.63° (EtOH).

erythro-(2*S*,3*R*)-2-(Benzoyloxy)-3-chlorobutane (**50b**): $[\alpha]^{20}_D$ +5.67° (EtOH). Addition of a chiral shift reagent, $Eu(TFC)_3$, to a $CDCl_3$ solution of compound **50b** indicated the presence of only one enantiomer. However, the small shift difference of the enantiomers prevented a more accurate determination of the isomeric composition. Compound **51** was obtained in 81% yield by treatment of compound **50b** with potassium pentylate in 1-pentanol, following the procedure by Högberg[26] for the preparation of *trans*-(2*S*,3*S*)-2,3-epoxybutane from (2*S*,3*R*)-2-acetoxy-3-bromobutane. The epoxide was distilled together with some 1-pentanol (cooling to −78 °C). Its optical rotation was determined in 1-pentanol and compared with an authentic sample. The enantiomeric excess was >90% ee ($[\alpha]^{20}_D$ −40.6° (1-pentanol) for the pure *trans*-(2*S*,3*S*)-2,3-epoxybutane).

Dechlorotelluration of Ditellurides with Cu(0). Typical Procedure: Allyl Benzoate from Bis(2-(benzoyloxy)-3-chloropropyl) Ditelluride (7a). Compound **7a** (0.35 g, 0.54 mmol) was heated to reflux in dioxane (30 mL) containing copper powder (0.50 g, 7.9 mmol) for 45 min (colorless solution). The black Cu/CuTe was then filtered off and the solvent evaporated. The residue was extracted with ethyl ether, washed with water, dried, and evaporated. Filtration through a short silica column afforded 0.16 g (91%) of allyl benzoate.

The following conversions were performed in a similar way (yield in parentheses): **7d** → allyl cinnamate (93%); **15** → methallyl benzoate (66%); **16** → crotyl benzoate (58%); **17** → α-methylallyl benzoate (97%); **18** → α,α-dimethylallyl benzoate (67%).

Acknowledgment. An authentic sample of *trans*-(2*S*,3*S*)-2,3-epoxybutane was kindly provided by Dr. Hans-Erik Högberg, Högskolan i Sundsvall/Härnösand, Sundsvall, Sweden. Financial support by the Swedish Natural Science Research Council is gratefully acknowledged.

Registry No. 4a, 90270-10-3; **4b**, 90270-11-4; **4c**, 90270-12-5; **4d**, 90270-13-6; **4e**, 90270-14-7; **4f**, 90270-15-8; **4g**, 90270-16-9; **7a** (isomer 1), 90270-17-0; **7a** (isomer 2), 90270-44-3; **7b**, 90270-18-1; **7c**, 90270-19-2; **7d**, 90270-20-5; **10a**, 90270-21-6; **10b**, 90270-22-7; **11**, 90295-40-2; **12**, 90270-23-8; **13**, 90270-24-9; **14**, 90270-25-0; **15**, 90270-26-1; **16**, 90270-27-2; **17**, 90270-28-3; **18**, 90270-29-4; **21**, 13997-70-1; **22**, 14593-43-2; **23**, 90270-30-7; **24**, 90270-31-8; **25**, 18203-32-2; **26**, 90270-32-9; **28**, 10283-95-1; **32**, 90270-33-0; **33**, 85021-16-5; **34**, 90270-34-1; **36**, 90270-35-2; **37**, 90270-36-3; *erythro*-**44**, 90270-37-4; **45**, 90270-38-5; **46**, 90270-39-6; **47**, 90270-40-9; *erythro*-**48**, 90270-41-0; **49**, 6118-13-4; **50a**, 90364-60-6; **50b**, 90364-61-7; **51**, 63864-69-7; **52**, 90270-42-1; $TeCl_4$, 10026-07-0; CH_2=$CHCH_2OH$, 107-18-6; $Cl_3TeCH_2CH(OH)CH_2Cl$, 90270-36-3; (*S*)-CH_2=$CHCH(CH_3)OC(O)Ph$, 90270-43-2; CH_2=$CHCH_2OC(O)Ph$, 583-04-0; CH_2=$CHCH_2OC(O)$-*p*-$C_6H_4CH_3$, 2653-46-5; CH_2=$CHCH_2OC(O)$-*p*-C_6H_4Cl, 15784-28-8; CH_2=$CHCH_2OC(O)$-*p*-$C_6H_4NO_2$, 15727-80-7; CH_2=$CHCH_2OC(O)CH_3$, 591-87-7; (*E*)-CH_2=$CHCH_2OC(O)CH$=$CHCH_3$, 5453-44-1; (*E*)-CH_2=$CHCH_2OC(O)CH$=$CHPh$, 56289-56-6; CH_2=$C(CH_3)CH_2OC(O)Ph$, 829-53-8; CH_2=$C(CH_3)CH_2OC(O)CH_3$, 820-71-3; (*E*)-CH_3CH=$CHCH_2OC(O)Ph$, 88927-00-8; CH_2=$CHCH(CH_3)OC(O)Ph$, 65001-62-9; CH_2=$CHC(CH_3)_2OC(O)Ph$, 31398-79-5; CH_2=$CHCH(Et)OC(O)Ph$, 52513-05-0.

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