

Tellurium Tetrachloride: Addition to Cyclohexene and Preparation from Tellurium Dioxide and Trimethylchlorosilane

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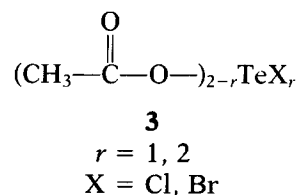
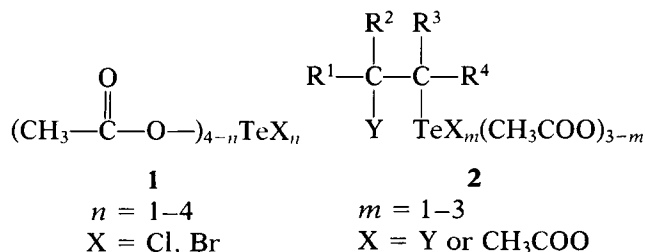
ABSTRACT

Tellurium dioxide, trimethylchlorosilane, acetyl chloride, or acetyl bromide in glacial acetic acid generated a homogeneous solution. Addition of cyclohexene produced trans-2-halocyclohexyl tellurium trihalides of excellent purity in 70% yield. With dichloromethane or ethanol-free chloroform the same compounds were obtained from heterogeneous reaction mixtures. trans-2-Methoxycyclohexyl tellurium trichloride was obtained quantitatively from tellurium dioxide, trimethylchlorosilane, and cyclohexene in absolute methanol. In the absence of cyclohexene, tellurium tetrachloride was obtained in 91% yield from tellurium dioxide and trimethylchlorosilane in chloroform, and tellurium tetrabromide in 98% yield from tellurium dioxide and acetyl bromide in glacial acetic acid.

INTRODUCTION

Oxirane's glycol process [1-3] reported in 1969 converts ethylene to 1,2-dihydroxyethane in a one-pot reaction that is catalyzed by a tellurium compound. The tellurium compound is formed by mixing tellurium dioxide, lithium chloride, and acetic acid. Subsequently, the usefulness of tellurium(IV) compounds as oxidizing agents for organic molecules was explored [4-8]. In these reactions, car-

ried out in acetic acid in the presence of lithium chloride [5] or lithium bromide [4,6] and catalytic amounts of tellurium dioxide, alkenes were oxidized with molecular oxygen to vic-diacetates [4-7], and conjugated dienes to 1,4-diacetoxyalk-2-enes [8]. The reported speculations about the mechanism of these reactions [4-8] generally lack experimental support. The tellurium(IV) species in the TeO₂-LiX-CH₃COOH system is proposed to be a mixed Te(IV) acetate halide (**1**) that electrophilically attacks the alkene to form a β-halo- or β-acetoxyalkyl tellurium(IV) intermediate (**2**). Oxidative cleavage of the Te-C bond in the intermediate **2** leads to the observed products.



The exact nature of the soluble tellurium(IV) acetate halide **1** is not known, evidence for the presence of the intermediate **2** is not available, and the role of the lithium halide in these reactions is obscure. The success of such tellurium-catalyzed re-

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actions, on which the Oxirane process is based, depends on the reactivities of the intermediate **2** and the properties [9] of the Te(II) compound **3** that must be extruded from **2** when the 1,2-disubstituted ethane is formed. The reactivities of the tellurium compounds **2** and **3** are influenced by the atoms and groups bonded to the olefinic carbon atoms and to the tellurium atom and by the solvent. Although the addition of tellurium tetrachloride to carbon-carbon double bonds has been investigated [10–16], no systematic study to delineate the influence of groups or atoms bonded to the olefinic carbons or to tellurium on the stability of the intermediate **2** and the chemical behavior of the divalent tellurium compound **3** has yet been carried out. Such studies would be easier to perform in homogeneous systems with solvents other than acetic acid in the absence of lithium halides. Unfortunately, tellurium tetrachloride is rather insoluble in common organic solvents and in acetic acid. Homogeneous solutions are obtained with acetic acid as solvent in the presence of lithium halides.

This contribution reports the formation of adducts between tellurium(IV) compounds and cyclohexene in the absence of lithium halides with chloroform, dichloromethane, methanol, or acetic acid serving as the reaction medium.

EXPERIMENTAL

Tellurium dioxide and trimethylchlorosilane were purchased from Aldrich Chemical Co. Cyclohexene, glacial acetic acid, acetyl chloride, dichloromethane, chloroform, and absolute methanol were ob-

tained from Fisher Scientific. Acetyl bromide was provided by Eastman Kodak Co.

trans-2-Halocyclohexyl Tellurium Trihalides by Addition of Tellurium Tetrahalides (Generated in Situ from Tellurium Dioxide) to Cyclohexene in Acetic Acid

Tellurium dioxide (0.80 g, 5.0 mmol), trimethylchlorosilane (2.20 g, 20 mmol), acetyl chloride (1.6 g, 20 mmol) or acetyl bromide (2.5 g, 20 mmol), and glacial acetic acid (10 mL) were placed into a 100-mL, nitrogen-flushed, round-bottom flask equipped with a magnetic stirrer and a reflux condenser. The mixture was stirred at room temperature or refluxed under a nitrogen atmosphere, until the tellurium dioxide had dissolved and the mixture had become homogeneous. Cyclohexene (0.80 g, 10 mmol) was then added. The mixture was stirred or refluxed for the period stated in Table 1. The white solid that had formed was collected by filtration, washed with a small amount of the solvent, and dried at room temperature under an oil-pump vacuum. The products were identified as *trans*-2-halocyclohexyl tellurium trihalides by proton and ¹³C NMR spectroscopy (Table 2). The yields and melting points are listed in Table 1.

trans-2-Chlorocyclohexyl Tellurium Trichloride from Tellurium Dioxide, Trimethylchlorosilane, and Cyclohexene in Dichloromethane or Chloroform

A mixture of tellurium dioxide (0.80 g, 5.0 mmol), trimethylchlorosilane (2.20 g, 20 mmol), and dichloromethane or ethanol-free chloroform was re-

TABLE 1 Preparation of 2-Y-Cyclohexyl Tellurium Trihalides from Cyclohexene, Tellurium Dioxide, and Trimethylchlorosilane or Acetyl Halides^a

			Product		
RX	Solvent	Conditions	X	Y	Yield, (%) ^b
(CH ₃) ₃ SiCl	CH ₃ COOH	Room temp., 1 hr	Cl	Cl	70 ^c
(CH ₃) ₃ SiCl	CHCl ₃	Reflux, 1 hr	Cl	Cl	72 ^c
(CH ₃) ₃ SiCl	CH ₂ Cl ₂	Reflux, 1 hr	Cl	Cl	54 ^c
(CH ₃) ₃ SiCl	CH ₃ OH	Reflux, 1 hr	Cl	CH ₃ O	100
CH ₃ COCl	CH ₃ COOH	Room temp., 1 hr	Cl	Cl	68 ^c
CH ₃ COBr	CH ₃ COOH	Room temp., 1 hr	Br	Br	70

^a Cyclohexene, 10 mmol; TeO₂, 5.0 mmol; RX, 20 mmol; solvent, 10 mL.
^b Yield based on TeO₂.
^c mp, 112°C.

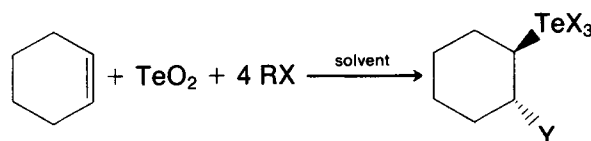
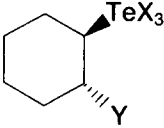


TABLE 2 Proton and ^{13}C NMR Data for *trans*-2-Y-Cyclohexyl Tellurium Trihalides in CDCl_3



X	Y	H—C—Te	H—C—Y	Other cyclohexane	CH_3O
Cl	Cl	3.93 (dt) 11.6 ^a , 4.7 ^b 82.7 ^c	4.30 (dt) 11.0 ^a , 4.0 ^b 61.8	1.3–2.7 (m) 25.0, 26.5, 27.7, 37.8	
Br	Br	5.03 (dt) 11.6 ^a , 4.0 ^b 79.0 ^c	5.20 (dt) 11.6 ^a , 4.2 ^b 55.6	1.4–2.8 (m) 26.3, 27.3, 30.5, 38.7	
Cl	CH_3O	4.71 (dt) 11.6 ^a , 4.0 ^b 80.6 ^c	4.90 (dt) 11.6 ^a , 4.0 ^b 78.6	1.5–2.8 (m) 22.9, 25.8, 27.6, 32.3	57.5 (s)

^a $J_{\text{H}(\text{CTeX}_3)-\text{H}(\text{CY})}$.
^b $J_{\text{H}_2\text{C}-\text{CH}(\text{TeX}_3\text{ or CY})}$.
^c Carbon-13 shifts.

fluxed under a nitrogen atmosphere for 1 h. Cyclohexene (0.40 g, 5.0 mmol) was then added to the white suspension. The mixture was refluxed for 2 h. During this time the amount of suspended solid decreased, but the mixture remained heterogeneous. The mixture was cooled to room temperature and then filtered. Evaporation of the solvent under an aspirator vacuum at room temperature left a white solid that was dried under an oil-pump vacuum at room temperature. The product (1.22 g, 70% yield) melted at 110–112°C and gave the same NMR spectrum as the compound isolated from the reaction in acetic acid.

trans-2-Methoxycyclohexyl Tellurium Trichloride from Tellurium Dioxide, Trimethylchlorosilane, and Cyclohexene in Methanol

A mixture of tellurium dioxide (0.80 g, 5.0 mmol), trimethylchlorosilane (2.20 g, 20 mmol), and absolute methanol (5 mL) was stirred and refluxed under an atmosphere of nitrogen in a 100-mL round-bottom flask equipped with a magnetic stirrer and a reflux condenser. After 10 min a yellow, homogeneous solution had formed. Cyclohexene (0.40 g, 5.0 mmol) was added. The mixture was refluxed for 1 h and then cooled to room temperature. A small amount of solid was separated by filtration. The solvent was evaporated from the filtrate under an aspirator vacuum at room temperature. The remaining yellow oil (1.74 g, 100% yield), which could not be induced to crystallize, was identified by NMR spectroscopy as *trans*-2-methoxycyclohexyl tellurium trichloride.

Tellurium Tetrachloride

Tellurium dioxide (2.4 g, 15 mmol) and trimethylchlorosilane (6.6 g, 61 mmol) were added to ethanol-free chloroform (15 mL) kept in a 100-mL nitrogen-flushed, round-bottom flask equipped with a magnetic stirrer and a reflux condenser. The mixture was stirred and refluxed under an atmosphere of dry nitrogen. The tellurium dioxide slowly dissolved. White tellurium tetrachloride began to precipitate from the homogeneous solution. After a 3-h reflux period the mixture was cooled to room temperature and then quickly filtered to avoid contact of the tellurium tetrachloride with moist air. The filter cake was washed several times with dichloromethane and then dried under an oil-pump vacuum at room temperature. The dry tellurium tetrachloride weighed 3.7 g (91% yield). After sublimation under an oil-pump vacuum in an oil bath at 200°C the tellurium tetrachloride melted at 220–222°C (lit. [17], 224°C).

Tellurium Tetrabromide

Glacial acetic acid (10 mL) was placed in a 100-mL Erlenmeyer flask containing a magnetic stirring bar. Tellurium dioxide (0.80 g, 5.0 mmol) and acetyl bromide (2.5 g, 20 mmol) were added. The mixture was stirred at room temperature. The mixture became homogeneous and then a yellow-orange precipitate formed. After the mixture had been stirred for 3 h, it was filtered. The filter cake was washed with a small amount of glacial acetic acid and then dried under an oil-pump vacuum at room

temperature. The orange tellurium tetrabromide (2.2 g, 98% yield) did not melt below 200°C.

Addition of Tellurium Tetrachloride to Cyclohexene

Tellurium tetrachloride (1.35 g, 5.0 mmol), isolated from the reaction of tellurium dioxide with trimethylchlorosilane in chloroform, was suspended in a 50-mL Erlenmeyer flask in chloroform (10 mL) under an atmosphere of dry nitrogen. Cyclohexene (0.41 g, 5.0 mmol) was added to the suspension. The mixture was stirred at room temperature for 1 h. At that time almost all of the tellurium tetrachloride had reacted. The mixture was filtered to remove a small amount of solid from the colorless solution. The filtrate was stripped of the solvent. The solid residue (1.55 g, 88% yield) was washed with glacial acetic acid and dried at room temperature under an oil-pump vacuum. The product, *trans*-2-chlorocyclohexyl tellurium trichloride, melted at 112°C and gave the same NMR spectrum as the compound prepared from $\text{TeO}_2-(\text{CH}_3)_3\text{SiCl}-\text{CH}_3\text{COOH}$.

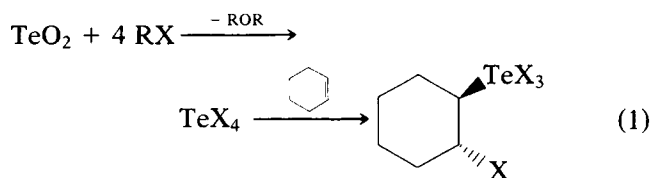
Addition of Tellurium Tetrabromide to Cyclohexene

Tellurium tetrabromide (2.24 g, 5.0 mmol), prepared from tellurium dioxide and acetyl bromide, was suspended in glacial acetic acid (10 mL). Cyclohexene (0.41 g, 5.0 mmol) was added. The mixture was stirred at room temperature for 1 h. The yellow precipitate, *trans*-2-bromocyclohexyl tellurium tribromide, was collected by filtration and recrystallized from a mixture of hexane-chloroform; yield, 1.19 g, 3.6 mmol, 72%. This product had the same properties as the compound prepared from $\text{TeO}_2-\text{CH}_3\text{COBr}-\text{CH}_3\text{COOH}$.

RESULTS AND DISCUSSION

During the search for homogeneous systems in which a tellurium(IV) compound would add to an olefin in the absence of a lithium halide, trimethylchlorosilane, acetyl chloride, and acetyl bromide were found to serve as a convenient source of halogens for the conversion of tellurium dioxide to a tellurium(IV) halide. When a suspension of tellurium dioxide in acetic acid and four or more molar equivalents of trimethylchlorosilane, acetyl chloride, or acetyl bromide were stirred at room temperature or refluxed, the tellurium dioxide began to react forming a soluble product. A homogeneous solution was soon obtained. When fewer than four molar equivalents of the halogen compounds were used, some tellurium dioxide remained in suspension. Addition of twice the stoichiometrically required amount of cyclohexene led to the formation of *trans*-2-halocyclohexyl tellurium trihalides in 70% yield. The additions were *anti*-stereospecific as indicated by the vicinal proton coupling constants

of 11 Hz [12] (Table 2). The isolation of *trans*-2-halocyclohexyl tellurium trihalides suggests that tellurium dioxide is first converted to a tellurium tetrahalide, which subsequently adds to the C=C double bond in *trans* fashion:



where if $\text{R} = \text{CH}_3\text{CO}$, $\text{X} = \text{Cl}, \text{Br}$; if $\text{R} = (\text{CH}_3)_3\text{Si}$, $\text{X} = \text{Cl}$. The high yields (70%) of isolated *trans*-2-halocyclohexyl tellurium trihalides are surprising, because under very similar conditions but with lithium bromide as the halogen source no 2-bromocyclohexyl tellurium tribromide was detected [7]. The reaction of tellurium tetrabromide and cyclohexene in refluxing glacial acetic acid (2 h) produced a black suspension, from which a mixture of *trans*-1,2-dibromocyclohexane and *trans*-1,2-diacetoxycyclohexane, but no *trans*-2-bromocyclohexyl tellurium tribromide, was isolated [7]. Under the conditions identified in Table 1 neither the halogen nor the TeX_3 group is replaced by the acetoxy group. Therefore, these conditions are well suited to the preparation of pure *trans*-2-halocyclohexyl tellurium trihalides. These compounds were identified by proton and ^{13}C NMR spectroscopy (Table 2) and by their melting points. *trans*-2-Chlorocyclohexyl tellurium trichloride melts at 111–114°C [11,18] (Table 1). The reported melting point of 122–124°C [12] appears to be a typing error.

When the reaction between tellurium dioxide, trimethylchlorosilane, and cyclohexene was carried out in refluxing dichloromethane or ethanol-free chloroform, the reaction mixtures remained heterogeneous but produced nevertheless *trans*-2-chlorocyclohexyl tellurium trichloride in acceptable yield and purity (Table 1). With dry methanol as solvent and trimethylchlorosilane as halogen source a homogeneous solution was soon formed. Addition of cyclohexene produced quantitatively *trans*-2-methoxycyclohexyl tellurium trichloride, an oily substance that was identified by NMR spectroscopy.

The reaction of tellurium dioxide with trimethylchlorosilane, acetyl chloride, or acetyl bromide is a convenient method for the preparation of tellurium tetrachloride and tellurium tetrabromide. Tellurium dioxide and four molar equivalents of trimethylchlorosilane in refluxing ethanol-free chloroform produced tellurium tetrachloride as a white precipitate in 91% yield in excellent purity. If desired, the tellurium tetrachloride can be purified by sublimation at 200°C under an oil-pump vacuum. Tellurium tetrachloride could not be isolated when tellurium dioxide and acetyl chloride were reacted in glacial acetic acid. However,

tellurium tetrabromide was obtained as an orange precipitate under these conditions with acetyl bromide as the halogen source. The tellurium tetrachloride and tellurium tetrabromide prepared in this way added cleanly to cyclohexene in glacial acetic acid, producing *trans*-2-halocyclohexyl tellurium trihalides. Elemental tellurium did not form in any of these reactions. Earlier reports [7] on similar reactions state that the reaction mixtures blackened as the reactions proceeded.

The reaction systems described allow 2-Y-cyclohexyl tellurium trihalides to be prepared from cyclohexene in good yields and high purity using tellurium dioxide that is much easier to handle than tellurium tetrahalides as the tellurium-containing starting material. Acetic acid, chloroform, and dichloromethane are solvents that generate either homogeneous reaction mixtures or sufficiently high concentrations of intermediates and products to make NMR studies of these reactions feasible. The NMR-silent lithium halides are replaced by trimethylchlorosilane, or acetyl halides as the halogen sources. In the absence of cyclohexene, tellurium tetrachloride or tellurium tetrabromide are obtained. This procedure is easier to carry out than the reaction of tellurium with chlorine or bromine [17].

Acknowledgments

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