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Tellurium Dioxide-Catalyzed Chlorination of Alcohols with Chlorotrimethylsilane

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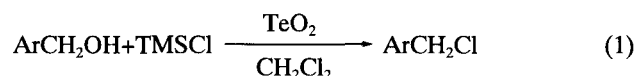
Received June 15, 1997

Recently, Palomo and Aizpura¹ reported that chromic anhydride easily react with chlorotrimethylsilane in methylene chloride forming a dark red chromium oxidizing agent. This neutral reagent was proved to be efficient for the oxidation of secondary alcohols to ketones, thiols to disulfides, and oximes to the corresponding carbonyl compounds.¹ A simple insertion of chromic anhydride into silicon-chlorine bond of chlorotrimethylsilane would produce trimethylsilylchlorochromate which Palomo *et al.* proposed as an active oxidant.¹ In the study on the insertion reaction of inorganic compounds to reactive silicon-halogen bond, we reported some valuable reactions for the oxidation of toluenes,² alcohols³ and olefins⁴ and chlorinations of alcohols.⁵

Halosilanes were known to be useful for halogenation of alcohols. Silicon tetrachloride can convert reactive alcohols to the corresponding chlorides at high temperature.^{6,7} Reactive iodotrimethylsilane also converts primary alcohols to alkyl iodides under mild conditions.⁸ Bromotrimethylsilane requires a higher temperature to react with primary alcohols to produce alkyl bromides.⁹ Use of chlorotrimethylsilane generally fails to produce alkyl chlorides. There are a few reports on the use of chlorotrimethylsilane for the preparation of alkyl chlorides.¹⁰ Potassium carbonate¹¹ and bismuth (III) chloride¹² were known to activate the chlorinating power of chlorotrimethylsilane, but the former is appeared to be limited to some reactive allylic alcohols.¹¹ Dimethylsulfoxide catalyzed chlorotrimethylsilane was known to convert primary and tertiary alcohols to the corresponding chlorides.¹³ Selenium dioxide was known to react with chlorotrimethylsilane to produce insertion products.¹⁴ A trimethylsilylchloroselenite was displaced rapidly by a chloride, forming selenium(IV) oxodichloride. The selenium(IV) oxodichloride generated *in situ* from the reaction of selenium dioxide and chlorotrimethylsilane is known to convert various alcohols into corresponding chlorides.¹⁴

Taking into account the structural similarity of tellurium

(IV) oxodichloride to those chlorinating agents such as thionyl chloride and selenium(IV) oxodichloride, we expected that tellurium(IV) oxodichloride can be developed as a new chlorinating agent for many organic functional groups. Indeed, when benzyl alcohol was treated with 2 equivalents of chlorotrimethylsilane and one equivalent of tellurium dioxide, the reaction was complete within an hour at room temperature (Equation 1).¹⁵ The conversion was almost quantitative without any side products in the reaction mixtures.



A number of examples of the chlorination are summarized in Table 1. For most alcohols, the yields were almost quantitative. The conversion can be easily achieved in the chlorinated solvents such as methylene chloride or carbon tetrachloride of an alcohol and chlorotrimethylsilane containing tellurium dioxide. Most of primary alcohols as well as benzylic alcohols were chlorinated efficiently without any skeletal rearrangement and competing side reactions such as elimination. Cyclic alcohols and other secondary alcohols were also easily converted into the corresponding alkyl chlorides without rearrangement of carbon skeleton. Conversion of tertiary alcohols into corresponding chlorides were appeared to have some problems due to competing elimination. Allylic alcohol such as *trans*-cinnamyl alcohol also produced allylic chloride at room temperature without any side reactions.

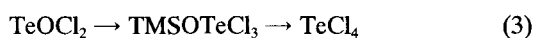
This reaction was found during the course of our study of the functional group transformations using inorganic oxides/organosilanes.²⁻⁵ Tellurium dioxide first reacts with chlorotrimethylsilane to form trimethylsilyloxytellurium(IV) oxochloride which rapidly decomposes into tellurium(IV) oxodichloride (Equation 2). The unstable tellurium(IV) oxodichloride reacts with another molecule of chlorotrimethylsilane to form tellurium tetrachloride eventually (Equation 3).

Table 1. Tellurium dioxide-catalyzed chlorination of alcohols with chlorotrimethylsilane

Reactants	Reaction Time (min.) ^a	Products	Yield ^b (%)
Benzyl alcohol	40	Benzyl chloride	96
4-Methoxybenzyl alcohol	30	4-Methoxybenzyl chloride	98
4-Methylbenzyl alcohol	40	4-Methylbenzyl chloride	97
1-Octanol	50	1-Chlorooctane	95
Neopentyl alcohol	50	Neopentyl chloride	96
2-Hexanol	40	2-Chlorohexane	98
2-Octanol	50	2-Chlorooctane	93
4-Heptanol	40	4-Chloroheptane	95
Cyclohexanol	50	Chlorocyclohexane	93
Cinnamyl Alcohol	50	Cinnamyl chloride	95
Borneol	40	Bornyl chloride	96
<i>t</i> -Butyl alcohol	40	<i>t</i> -Butyl chloride	93

^a Room temperature. ^b Isolated yield

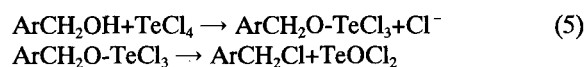
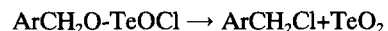
Actual structure of tellurium(IV) oxodichloride was known to have a form of $\text{Te}_6\text{O}_{11}\text{Cl}_2$ which is known to be formed by reaction of tellurium dioxide with tellurium tetrachloride.^{16,17} However, the structure of *in situ* generated tellurium(IV) oxodichloride is considered as the same that of selenium(IV) oxodichloride. We did not try to isolate the tellurium(IV) oxodichloride.



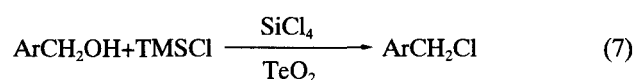
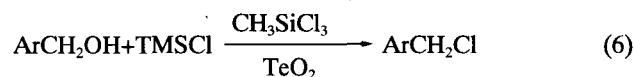
NMR spectrum of this nearly homogeneous insertion product showed only two types of singlet due to the methyl protons of excess chlorotrimethylsilane and hexamethyldisiloxane. No NMR peak other than these two types of protons was observed. This means that insertion product of trimethylsilyloxytellurium(IV) oxochloride can exist only as transient species. The ratio of methyl protons of chlorotrimethylsilane and hexamethyldisiloxane did not vary on standing or on heating the mixture for several hours. All these steps are believed to be reversible and are in equilibrium. The *in situ* generated tellurium(IV) species could be used to convert various alcohols to the corresponding chlorinated compounds.

Tellurium tetrachloride is known to be white, volatile, hygroscopic, readily hydrolysable solids, and fairly soluble in non-polar organic solvents.¹⁷ Tellurium tetrachloride^{17,18} is known to readily aromatize unsaturated or halogenated cyclic or polycyclic hydrocarbons. Aromatic compounds are also known to be chlorinated by tellurium tetrachloride. Tellurium tetrachloride has also a Lewis acid properties acting catalyst when aldehydes and ketones react with alkanethiols.^{17,18}

The mechanism for the chlorination could be proposed as shown in equation 4 and 5, respectively. These chlorination reaction can be better understood, when one considers the structure of tellurium(IV) oxodichloride compared selenium(IV) oxodichloride which was known to be a useful chlorinating agent for a wide variety of alcohols.¹⁴



Dichlorodimethylsilane or trichloromethylsilane (Equation 6) were also useful for converting benzylic alcohols to the corresponding chlorides in the presence of tellurium dioxide. Combination of silicon tetrachloride and tellurium dioxide was also effective for chlorination (Equation 7). From benzyl alcohol, benzyl chloride was obtained in quantitative yield at room temperature. 4-Methylbenzyl chloride was obtained from 4-methylbenzyl alcohol in high yield at room temperature. Allylic chloride such as cinnamyl chloride was also obtained in high yield from *trans*-cinnamyl alcohol.



In summary, these *in situ* generated tellurium(IV) oxodichloride and tellurium tetrachloride were found to be very effective for the chlorination of a wide variety of alcohols. Although, much work remains to be done to understand detailed aspects of the reaction, these tellurium reagents generated *in situ* will be a valuable addition to the list of chlorinating agents for alcohols to the corresponding chlorides. We are currently trying to characterize the nature of actual chlorinating species and to apply the chlorination of other functional groups.

Acknowledgment. This work was supported by the Suncheon National University (1996 Fund).

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 - The reaction of benzyl alcohol is representative. A well-dried 100 ml two-necked flask equipped with a reflux condenser and oil bubbler was placed 0.02 mole of chlorotrimethylsilane and 0.01 mole of tellurium dioxide in 15 mL of methylene chloride. After several minutes stirring at room temperature, the mixture changed into a homogeneous pale yellow solution. And 0.01 mole of benzyl alcohol diluted in 5 mL methylene chloride was slowly added dropwise to the above mixture, and the resulting reaction mixture was stirred for 1 hour at room temperature. TLC observation (eluent: methylene chloride/carbon tetrachloride) and NMR spectrum of the crude reaction mixture showed complete conversion to benzyl chloride. The reaction mixture was filtrated through a silica gel (70-230 mesh) column and the solvent was removed using a rotary evaporator. The product was identical in all respects with the authentic benzyl chloride.
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XANES Study on the Structural Conformation of Fe Ions

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Received June 27, 1997

The XANES (X-ray absorption near-edge structure) gives information on the coordination geometry as well as that of the electronic configuration around the Fermi level of absorbing atoms. Several research groups have reported that the XANES spectra show various features according to the coordination number by study on the XANES spectra of Fe ions existing in various complexes.¹⁻⁴ Though the iron ions exist at various sites with nearly the same local symmetry and in the same valence state, they exhibit significantly different XANES features.

Insofar as both structural and electronic changes are intimately correlated, the origin of the strong XANES modification at the iron K-edge is not obvious. Therefore, to understand the nature of the modifications, we have studied XANES of the Fe ions located at various sites. We present various Fe K-edge XANES features for spinel, perovskite, and K₂NiF₄ type compounds, and try to explain the various XANES features by using multiple scattering.

The crystallographic structures of ZnFe₂O₄ and GeFe₂O₄ are assigned to cubic spinel type structure with the space group of *Fd3m* identified by analysis of XRD patterns. For the spinel structure, the cubic close packed oxygen ions form two different sites such as tetrahedra and octahedra which can be filled by the metal ions.⁵ It is confirmed by the Mössbauer spectroscopic analyses that the valence states of Fe ions in ZnFe₂O₄ and GeFe₂O₄ are 3+ and 2+, respectively, and all of the Fe ions exist in octahedral site.

The LaFeO₃ and LaSrFeO₄ compounds are identified as perovskite and K₂NiF₄ type structures, respectively. The oxidation state of Fe ions for the LaFeO₃ and LaSrFeO₄ is trivalent and the ions are octahedrally coordinated with six ox-

ygens. The representative K₂NiF₄-type compound shows tetragonal system with the *I4/mmm* space group which is composed of rock salt and perovskite layers alternately.^{6,7} The D_{4h} distortion of FeO₆ octahedra takes place due to the relatively weak interplanar interaction along the crystallographic *c* axis between the magnetic ions in K₂NiF₄-type LaSrFeO₄ compounds. Lattice parameters of the LaSrFeO₄ compound are *a*=3.851(2) and *c*=12.65(4) Å and thus the tetragonality (*c/a*) is 3.29. Ca₂Fe₂O₅ is a brownmillerite type structure and its space group is *Pcmm*. Mössbauer spectrum of Ca₂Fe₂O₅ shows that the unit cell consists of alternating sheets of octahedra (FeO₆) and tetrahedra (FeO₄) in the crystallographic *b* direction.⁸ The crystallographic data for the samples in this study are summarized in Table 1.

The Fe K-edge XANES spectra of the compounds have been recorded at the BL-6B of Photon Factory, National Laboratory for the High Energy Physics (KEK-PF) in Japan. Synchrotron radiation from the storage ring has been monochromatized with a Si(1 1 1) channel-cut monochromator. The spectra were calibrated with respect to the first inflection point of a Fe-foil. The data were monitored with a step size of < 0.3 eV in the XANES region.

Figure 1 shows the normalized Fe K-edge XANES spectra for ZnFe₂O₄, GeFe₂O₄, LaFeO₃, LaSrFeO₄, and Ca₂Fe₂O₅. The pre-edge peak denoted as P around 7110 eV is assigned to the formally dipole-forbidden 1s → 3d transition.⁹⁻¹² Since the peak gains its intensity from the quadrupole allowed transition in the octahedral symmetry, the observed pre-edge intensity for the compounds except Ca₂Fe₂O₅ is very weak. However, the pre-edge peak of Ca₂Fe₂O₅ with tetrahedrally coordinated iron ions gains strong intensity due to mix-