# Photosensitized oxygenation of diaryl tellurides to telluroxides and their oxidizing properties

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Photosensitized oxidation of tellurides carrying bulky aromatic substituents afforded the corresponding telluroxides which were found to react with simple alcohols to give the corresponding carbonyl compounds in excellent yields along with the starting tellurides.

Recently, along with public awareness of environmental issues there is growing need for the introduction of clean synthesis. The necessity for a better reagent for oxidation reactions in organic synthesis led us to introduce here bulky diaryl telluroxides which, due to the weak tellurium–oxygen bond, are expected to efficiently transfer the oxygen atom to organic substrates. Diaryl telluroxides, in particular 4,4′-dimethoxydiphenyl telluroxide **2c**, are recognized as mild and selective oxidizing reagents for a number of organic substrates; however, the telluroxides do not react with simple alcohols.[1–3] It is well known that the telluroxides are prone to form an aggregate structure held together by tellurium–oxygen interactions[4] or to react with water to afford a hydrate.[5] Consequently, the intrinsic oxidizing ability of the telluroxide itself may not be exhibited. The bulky aryl substituents such as 2,4,6-trimethylphenyl (Mes) and 2,4,6-triisopropylphenyl (Tip) groups adopted for this work are expected to alter the equilibrium constants of such processes.

Generally, organic telluroxides are prepared by direct oxidation of the corresponding tellurides using *m*CPBA or NaIO$_4$ or by oxidative dihalogenation of the tellurides followed by alkaline hydrolysis. Availability of methods for converting the tellurides to telluroxides by molecular oxygen would provide an environmentally benign oxidation process employing organotellurium compounds as an oxygen atom transporter.

It was shown by Detty and coworkers that the organotellurium compounds act as a chemical quencher of singlet oxygen and afford the corresponding telluroxides or their hydrates.[6] However, there are no synthetic studies on the photosensitized formation of telluroxides from simple tellurides and molecular oxygen. In this paper, we describe photosensitized oxygenation of diaryl tellurides to the corresponding teluroxides and the first example of the oxidation of simple alcohols by chalcogen oxides.

Singlet oxygen oxidation of di(Mes) and di(Tip) tellurides **1a** and **1b** as well as simple tellurides **1c** and **1d** was carried out at room temperature for 1 h in ethanol using rose bengal as a photosensitizer to give the corresponding telluroxides **2a**,[7] **2b**, **2c** and **2d** in quantitative yields (Scheme 1). The use of ethanol as a solvent was essential for the clean formation of telluroxides. The protic solvents probably stabilize the pertelluroxide intermediate.[8] Compound **2b** was a new compound and was fully characterized by ¹H, ¹³C and ¹²⁵Te NMR, EI-MS and elemental analysis.†

The synthesis of optically active telluroxides bearing bulky aryl substituents by an alternative route has already been reported,[9] but reactivities of the bulky telluroxides have not yet been studied.
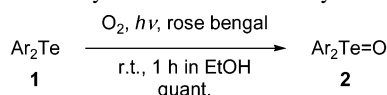
In order to check the reactivity of the bulky diaryl telluroxides as an oxidizing agent, we carried out the oxidation of triphenylphosphine with dimesityl telluroxide **2a** in chloroform at room temperature. After 2 h, ¹H NMR analysis of the reaction mixture revealed the formation of triphenylphosphine oxide in 77% yield. It was demonstrated by Ley and coworkers[1] that the oxidation of triphenylphosphine by 4,4′-dimethoxydiphenyl telluroxide **2c** required 48 h to obtain 80% yield of triphenylphosphine oxide.‡ Obviously, dimesityl telluroxide **2a** is a better oxidant than 4,4′-dimethoxydiphenyl telluroxide **2c**. These results prompted us to investigate the use of the bulky telluroxides **2a** and **2b** to effect the oxidation of simple alcohols.

When a solution of telluroxide **2a** and 4-bromobenzyl alcohol in *p*-xylene was refluxed for 3 h, almost quantitative formation (96%) of 4-bromobenzaldehyde was observed by direct analysis of the reaction mixture using ¹H NMR spectroscopy (Table 1, run 1). The spectrum also showed the quantitative recovery of the telluride **1a** and the absence of 4-bromobenzoic acid. A similar reaction in refluxing toluene required prolonged reaction time (16 h) to obtain satisfactory yield (93%). Oxidation of 4-bromobenzyl alcohol using di(Tip) telluroxide **2b** also proceeded smoothly to give 4-bromobenzaldehyde in 94% yield after 3 h (run 2); however, the reactions of 4,4′-dimethoxydiphenyl and diphenyl telluroxides **2c**

**Table 1** Oxidation of alcohol using diaryl telluroxide **2**[a]

| Run | Alcohol | Telluroxide | Time (h) | Product | Yield (%)[b] |
|---|---|---|---|---|---|
| 1 | 4-BrC$_6$H$_4$CH$_2$OH | **2a** | 3 | 4-BrC$_6$H$_4$CHO | 96 |
| 2 | 4-BrC$_6$H$_4$CH$_2$OH | **2b** | 3 | 4-BrC$_6$H$_4$CHO | 94 |
| 3 | 4-BrC$_6$H$_4$CH$_2$OH | **2c** | 3 | 4-BrC$_6$H$_4$CHO | 12 |
| 4 | 4-BrC$_6$H$_4$CH$_2$OH | **2d** | 3 | 4-BrC$_6$H$_4$CHO | 16 |
| 5 | PhCH$_2$OH | **2a** | 4 | PhCHO | 89 |
| 6 | 4-MeOC$_6$H$_4$CH$_2$OH | **2a** | 4 | 4-MeOC$_6$H$_4$CHO | 95 |
| 7 | 4-O$_2$NC$_6$H$_4$CH$_2$OH | **2a** | 2 | 4-O$_2$NC$_6$H$_4$CHO | 92 |
| 8 | 2,6-dichlorobenzyl alcohol | **2b** | 6 | 2,6-dichlorobenzaldehyde | 60 |
| 9 | Ph$_2$CHOH | **2a** | 4 | Ph$_2$C=O | 92 |
| 10 | PhCH(OH)Me | **2b** | 17 | PhC(O)Me | 32 |
| 11 | *trans*-2-dodecenol | **2b** | 6 | *trans*-2-dodecen-1-al | 70 |
| 12 | PhCH=CHCH$_2$OH | **2a** | 3 | PhCH=CHCHO | 89 |
| 13 | 1-octanol | **2a** | 23 | octanal | 0 |
| 14 | PhCH(OH)CO$_2$Me | **2b** | 4.5 | PhC(O)CO$_2$Me | 98 |
| 15[c] | HO-C$_6$H$_4$-OH | **2a** | 19 | O=C$_6$H$_4$=O | quant. |
| 16[d] | 1,2-bis(hydroxymethyl)benzene | **2a** | 6 | phthalide | 73 |
| | | | | 2-formylbenzaldehyde | 27 |

[a] All reactions were carried out in refluxing xylene using 1.2 equivalents of telluroxide unless otherwise noted. [b] Determined by ¹H NMR spectroscopy except for run 2 (determined by GC). [c] The reaction was carried out at room temperature in chloroform. [d] Three equivalents of telluroxide were used.



$$\text{Ar}_2\text{Te} \xrightarrow[\text{r.t., 1 h in EtOH} \atop \text{quant.}]{\text{O}_2, \ h\nu, \ \text{rose bengal}} \text{Ar}_2\text{Te=O}$$

**1** → **2**

**a**: Ar = 2,4,6-trimethylphenyl (Mes); **b**: Ar = 2,4,6-triisopropylphenyl (Tip)
**c**: Ar = 4-methoxyphenyl; **d**: Ar = Ph

**Scheme 1**

and **2d** with the alcohol for 3 h resulted in the formation of the corresponding aldehyde only in 12 and 16% yields, respectively (runs 3 and 4). The reason for the enhanced oxidizing ability of the bulky telluroxides is not clear at the present stage. We assume that the telluroxides **2a** and **2b** can exist as a monomeric form due to the bulky substituents, and, accordingly, the inherent reactivity of telluroxide itself, not as a hydrate or molecular aggregates, would be expressed. In fact, the $^{125}$Te NMR spectra of **2a** and **2b** in CDCl$_3$ at room temperature show signals at 1308 and 1314 ppm (relative to Me$_2$Te), respectively, which are far downfield as compared with those of diphenyl telluroxide **2d** (1035 ppm),[10] bis(pentafluorophenyl) telluroxide (1010 ppm)[4c] and tellurathiocin derivative (1154 ppm).[10] With the "true" telluroxide in hand, we examined the oxidation of a variety of alcohols. The representative results are also compiled in Table 1.

Benzyl alcohol and its 4-substituted derivatives having electron-donative and -withdrawing groups were efficiently oxidized with telluroxide **2a** to give the corresponding benzaldehydes in excellent yields (runs 5–7); however, 2,6-dichlorobenzyl alcohol suffered steric retardation to afford 2,6-dichlorobenzaldehyde in moderate yield (60%, run 8). While the oxidation of benzhydrol gave benzophenone in 92% yield (run 9), α-methylbenzyl alcohol was somewhat less reactive to afford acetophenone in 32% yield even after 17 h (run 10). Allylic alcohols such as *trans*-2-dodecenol (run 11) and cinnamyl alcohol (run 12) were also oxidized to the corresponding aldehydes in 70 and 89% yields, respectively, whereas saturated aliphatic alcohols such as 1-octanol (run 13) and cyclododecanol were entirely unreactive. Other hydroxy compounds such as methyl mandelate (run 14) and hydroquinone (run 15) were also converted to methyl benzoylformate and 1,4-benzoquinone in 98% and quantitative yields, respectively. With 1,2-benzenedimethanol, phthalide was obtained in 73% yield along with phthalaldehyde (27%) in the presence of three equivalents of **2a** (run 16), and the formation of phthalide can be explained by further oxidation of the intermediary hemiacetal. In all reactions, the bulkier telluroxide **2b** was equally effective as an oxidizing reagent and, in some cases, better yields were obtained by using the telluroxide **2b** (runs 8, 10, 11 and 14), where longer reaction time was needed to secure acceptable yields by using **2a**. For example, the oxidation of *trans*-2-dodecenol with **2a** afforded *trans*-2-dodecen-1-al in 43% yield even after 19 h. We speculate that the higher thermal stability of the telluroxide **2b** due to bulkier aryl substituents may be responsible for its enhanced reactivity.

In mechanistic consideration of the oxidation of alcohols, the pathway is postulated to be shown in Scheme 2. Namely, the alcohol attacks the tellurium–oxygen bond to give an adduct **A**



**Scheme 2**
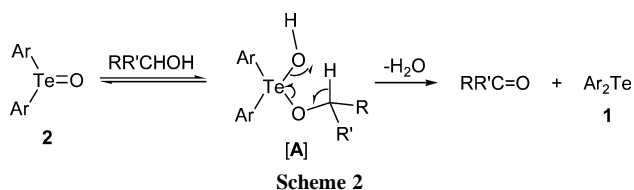
which undergoes intramolecular dehydration to afford the corresponding carbonyl compound and diaryl telluride **1**. The bulky substituents may also contribute to acceleration of the final reductive elimination due to the steric congestion around the tellurium(iv) atom. This is the first example of chalcogen oxide which can oxidize simple alcohols *via* a formal dehydrogenation reaction. An azeotropic removal of the liberated water by refluxing in xylene or toluene is essential to complete the reaction. When the oxidation of 4-bromobenzyl alcohol with **2a** was performed in a sealed tube, the yield of 4-bromobenzaldehyde was lowered to 65% even after 22 h. In all cases, the $^1$H NMR spectra of the reaction mixture revealed the quantitative formation of diaryl telluride **1**, indicating a catalytic process is feasible if re-oxidation of the recovered telluride can be performed in the same reaction system. Studies on the singlet oxygen oxidation of organic substrates using bulky diaryl telluroxides as a catalyst are currently under way.

## Notes and references

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