ORGANIC LETTERS

2009
Vol. 11, No. 9
1879−1881

# Aerobic Photooxidation of Phosphite Esters Using Diorganotelluride Catalysts

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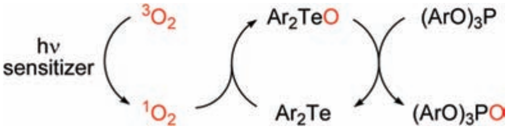
**Received February 4, 2009**

## ABSTRACT



**Diorganotellurides containing bulky aromatic substituents are found to catalyze the photooxidation of phosphite esters using aerobic oxygen as a terminal oxidant. A Hammett plot with substituted triaryl phosphites yielding $\rho = 2.88$ agrees with a nucleophilic oxygen transfer from telluroxide to phosphite.**

Oxidation reactions are a significant class of important and essential chemical processes. In general, such reactions are conducted using traditional inorganic and organic oxidants, such as dichromates, permanganates, organic peroxides, etc., stoichiometrically.[1] Recently, increasingly severe environmental constraints have generated greater interest in the use of environmentally benign molecular oxygen or hydrogen peroxide as oxidants.[2] Although oxidation of organic molecules by the ground-state triplet oxygen or hydrogen peroxide is thermodynamically favored, they are not kinetically competent to serve as an oxidant. Therefore, a large number of catalytic strategies have been proposed to achieve rate enhancement in the oxidation processes that have been developed.[3]

Direct oxygenation of an organic substrate through singlet oxygen via [2 + 2], [4 + 2], and ene additions is one of the most often used pathways in organic synthesis,[4] because the reaction rate of singlet oxygen is much greater than that of triplet oxygen as a result of its low activation energy. Furthermore, photosensitized oxygenations of organosulfur[5] and phosphorus[6] compounds have been extensively studied with respect to their synthetic and mechanistic aspects. However, reports explaining the use of singlet oxygen in catalytic systems are still scarce. It was demonstrated independently by Abatjoglou and Krief that diorganoselenides promoted the reoxidation of osmium(VI) to osmium(VIII) using singlet oxygen in the olefin dihydroxylation

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10.1021/ol900240s CCC: $40.75

reactions.[7] In this work, we focused on diorganotelluride catalysts. Detty and co-workers reported that singlet oxygen can efficiently oxidize diorganotellurides to give the corresponding telluroxides or their hydrates;[8] however, there have been no reports concerning their application to organic synthesis.

We have reported recently that photosensitized oxygenation of bulky diaryl tellurides produced corresponding telluroxides.[9] The diaryl telluroxides obtained were found to oxidize some organic substrates, and in some cases, the starting telluride was recovered quantitatively. These findings helped us to investigate the catalytic ability of diaryl tellurides in photooxygenation reactions. In this work, the catalytic photooxidation of phosphites in the presence of organotellurides is selected as an example to elucidate environmentally benign novel processes.

Initially, we investigated the catalytic photooxidation of triphenyl phosphite under various reaction conditions; the results are compiled in Table 1. When a 0.1 M acetonitrile solution of triphenyl phosphite containing bis(2,4,6-triisopropylphenyl) telluride ($Tip_2Te$, 1 mol %) was irradiated under aerobic conditions with a 500 W halogen lamp employing rose bengal (RB, $10^{-4}$ M) as a photosensitizer at 10−15 °C for 4 h, analysis of the reaction mixture by $^{31}P$ NMR spectroscopy showed a quantitative formation of triphenyl phosphate (run 1). Similar treatment in the dark, without a sensitizer, or in the absence of $Tip_2Te$ resulted in only a trace amount of phosphate formation or no reaction, indicating that the reaction involves singlet oxygen and that triaryl phosphite itself is completely unreactive toward singlet oxygen.

**Table 1.** Aerobic Photooxidation of Triphenyl Phosphite Catalyzed by Diaryl Telluride

$$(PhO)_3P \xrightarrow[h\nu,\ \text{sensitizer, air}]{\text{catalyst (1 mol \%)}} (PhO)_3PO$$

| run | catalyst | solvent (sens)[a] | time (h) | temp (°C) | yield (%)[b] |
|---|---|---|---|---|---|
| 1 | $Tip_2Te$ | $CH_3CN$ (RB) | 4 | 10−15 | quant |
| 2 | $Tip_2Te$ | $CH_3CN$ (RB) | 2.5 | 40−45 | quant |
| 3 | $Tip_2Te$[c] | $CH_3CN$ (RB) | 4 | 40−45 | 28 |
| 4 | $Tip_2Te$ | $C_5H_5N$ (HP) | 4 | 10−15 | quant |
| 5 | $Tip_2Te$ | $CH_2Cl_2$ (TPP) | 4 | 10−15 | 43 |
| 6 | $Tip_2Te$ | $CH_3OH$ (RB) | 4 | 10−15 | 15 |
| 7 | $Mes_2Te$ | $CH_3CN$ (RB) | 4 | 10−15 | 67 |
| 8 | $An_2Te$ | $CH_3CN$ (RB) | 4 | 10−15 | 14 |
| 9 | $Ph_2Te$ | $CH_3CN$ (RB) | 4 | 10−15 | 24 |

[a] RB, HP, and TPP denote rose bengal, hematoporphyrin, and tetraphenylporphyrin, respectively. [b] Determined by $^{31}P$ NMR spectroscopy. [c] 0.1 mol %.

Other diaryl tellurides, such as bis(2,4,6-trimethylphenyl) telluride ($Mes_2Te$), bis(4-methoxyphenyl) telluride ($An_2Te$), and diphenyl telluride, were also employed as a catalyst. The catalytic activity of $Mes_2Te$ was moderate, producing triphenyl phosphate in 67% yield (run 7), but $An_2Te$ and $Ph_2Te$ afforded the phosphate only in 14% and 24% yields, respectively (runs 8 and 9). The bulky aryl substituents on the tellurium atom are apparently responsible for increasing the catalytic activity.

A noticeable solvent effect was observed in this reaction. Although the use of pyridine as a solvent produced similar result affording triphenyl phosphate in quantitative yield (run 4), changing the solvent to dichloromethane decreased the reaction rate producing the phosphate in 43% yield after 4 h (run 5). In methanol solvent, the reaction retarded significantly producing triphenyl phosphate in 15% yield (run 6). In all solvents used, the isolated $Tip_2TeO$, the possible active species in this reaction (vide infra), could efficiently oxidize triphenyl phosphite. Therefore, the observed solvent effect is probably attributed to the efficiency of photosensitized formation of $Tip_2TeO$. At the present time, we cannot provide a clear explanation of the solvent effect because the mechanism of the singlet oxygen oxidation of $Tip_2Te$ would be very complex. Studies that address these issues are under investigation.

We found finally that carrying out the oxidation at an elevated temperature (40−45 °C) in acetonitrile solvent medium slightly improves the efficiency of the catalyst, and the reaction reached completion within 2.5 h (run 2). Efforts have been made to reduce the amount of catalyst; however, we could not obtain acceptable yields using 0.1 mol % of $Tip_2Te$ (run 3).

To explore the scope and limitation of the present method, the oxidation of a variety of phosphite esters was studied; the representative results are shown in Table 2. In the oxidation of triaryl phosphites, the presence of an electron-withdrawing *para* substituent, such as a chloro or trifluoromethyl group, resulted in an increase in reactivity producing corresponding phosphates in quantitative yields after 1 or 2 h, respectively (runs 2 and 3). However, an electron-donating methyl or methoxy group required somewhat longer

**Table 2.** $Tip_2Te$-Catalyzed Photooxidation of Phosphite Esters

$$(RO)_3P \xrightarrow[CH_3CN,\ 40\text{-}50\ ^{\circ}C,\ \text{air}]{Tip_2Te\ \text{(1 mol \%)},\ h\nu,\ \text{rose bengal}} (RO)_3PO$$

| run | $(RO)_3P$ | time (h) | yield (%)[a] |
|---|---|---|---|
| 1 | $(PhO)_3P$ | 2.5 | quant (92)[b] |
| 2 | $(4\text{-}ClC_6H_4O)_3P$ | 1 | quant |
| 3 | $(4\text{-}CF_3C_6H_4O)_3P$ | 2 | quant (94)[b] |
| 4 | $(4\text{-}MeC_6H_4O)_3P$ | 8 | quant |
| 5 | $(4\text{-}MeOC_6H_4O)_3P$ | 8 | quant (93)[b] |
| 6 | $(PhO)_2(MeO)P$ | 4 | 91 |
| 7 | $(PhO)(BuO)_2P$ | 4 | quant |

[a] Determined by $^{31}P$ NMR spectroscopy. [b] Isolated yield.

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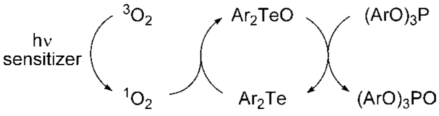
reaction time (8 h) to attain completion (runs 4 and 5). Mixed alkyl/aryl phosphite esters were also employed as substrates. Although $(PhO)_2POMe$ and $(BuO)_2POPh$ are moderately reactive toward singlet oxygen, $Tip_2Te$ addition improved the reaction efficiency affording the corresponding mixed phosphate esters in almost quantitative yields (runs 6 and 7). In the absence of $Tip_2Te$, $(PhO)_2(MeO)PO$ and $(PhO)(BuO)_2PO$ were obtained in 30% and 89% yields, respectively.

Various possible active species that may be involved in the transfer of an oxygen atom from singlet oxygen to phosphites are postulated. In particular, peroxytelluroxide ($Tip_2Te^+OO^-$), the initial intermediate perceived to be generated by the oxidation of $Tip_2Te$ through singlet oxygen, may oxidize phosphites. Its sulfur analog, $R_2S^+OO^-$,[10] is known to react with triphenyl phosphite.[11] In our case, we could not observe the reaction between $Tip_2Te^+OO^-$ and triphenyl phosphite individually because $Tip_2TeO$ also oxidizes the phosphite. Therefore, we tried to capture $Tip_2Te^+OO^-$ using $Ph_2SeO$, which is reported to be more reactive toward $R_2S^+OO^-$ than triphenyl phosphite.[12] However, we could not obtain any trapping product such as $Ph_2SeO_2$, indicating a rather low reactivity of $Tip_2Te^+OO^-$ intermediate. At the present state of this research, we assume that the $Tip_2TeO$, generated by the photosensitized oxygenation of $Tip_2Te$, acts as a main oxygen carrier (Scheme 1).

**Scheme 1.** Catalytic Cycle for Diorganotelluride-Catalyzed Oxidation of Phosphites with Singlet Oxygen



In fact, reaction of triphenyl phosphite with 1 equiv of the isolated $Tip_2TeO$ in acetonitrile at room temperature for 30 min afforded quantitative yields of triphenyl phosphate and $Tip_2Te$. The regeneration of $Tip_2Te$ is indispensable to complete the catalytic cycle in this process.

To obtain further insights into the reaction mechanism between phosphite and telluroxide, we invoked a conventional Hammett methodology.[13] Relative reactivities of substituted triaryl phosphites toward $Tip_2TeO$ were determined by competitive reaction using unsubstituted triphenyl phosphite and $^{31}P$ NMR spectroscopy. The plot of the logarithm of relative rate constants, $\log(k_X/k_H)$, against Hammett's $\sigma$-values exhibits a linear relationship (correlation coefficient $R^2 = 0.94$) with a reaction constant $\rho = 2.88$. The large positive slope indicates nucleophilic transfer of oxygen atom from telluroxide to phosphite and significant negative charge accumulation on the phosphorus atom in the transition state of the rate-determining step. Although a rational interpretation of this Hammett correlation in terms of charge distribution in the transition state awaits theoretical verification, we postulate the mechanism for the oxidation of phosphite ester by $Tip_2TeO$, as shown in Scheme 2. We propose that the attack of a negatively charged oxygen atom on the phosphorus atom generating a zwitterionic intermediate is rate-determining. Similar mechanisms are also proposed by Foote and Stratakis.[14]

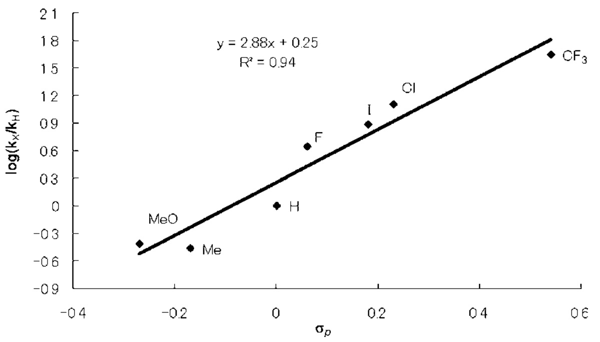
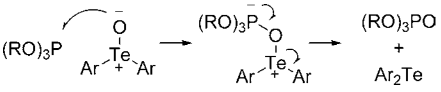


**Figure 1.** Hammett plot for the reaction of substituted triaryl phosphites with $Tip_2TeO$.

**Scheme 2.** Nucleophilic Oxygen Atom Transfer from $Ar_2TeO$ to $(RO)_3P$



In summary, we have elucidated the first instance of organotelluride-catalyzed photooxidation of phosphites using molecular oxygen as a terminal oxidant. This catalytic aerobic oxidation is very efficient, and further application of this catalytic system is under investigation.

**Acknowledgment.** Financial support from Tokai University is gratefully acknowledged.

**Supporting Information Available:** Experimental procedures and copies of NMR spectra for selected compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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