Aerobic Oxidation of Phosphite Esters to Phosphate Esters by Using an Ionic-Liquid-Supported Organotelluride Reusable Catalyst

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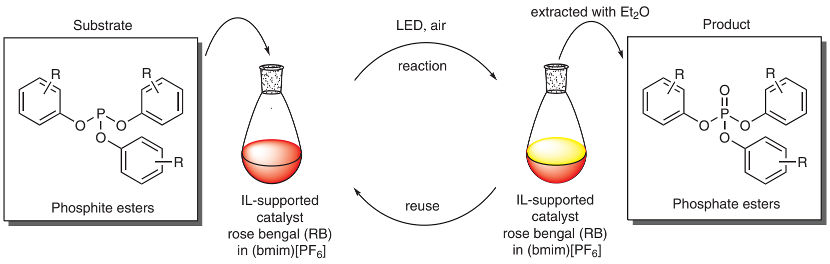

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Abstract We describe the synthesis of an ionic-liquid (IL)-supported organotelluride catalyst and its application as a recyclable catalyst for the aerobic oxidation of phosphite esters to phosphate esters. This method shows high conversion rates, allows the ready isolation and purification of the resulting products, and exhibits good reusability of the catalyst.

Keywords organotellurides, ionic liquids, oxidation, phosphate esters, reusable catalysts, phosphite esters

Phosphate esters, which are widely used in the chemical industry, can be obtained by the oxidation of phosphite esters.[1] Oxidations of phosphite esters to phosphate esters by using a quaternary phosphonium salt[2] or a borane[3] have been reported.

Organotellurium oxides are recognized as valuable oxidation catalysts. In one of our previous studies, we have achieved organotelluride-catalyzed oxidations of various substrates under photooxidation conditions, e.g., of silanes to silanols,[4] thiols to disulfides,[5] and alcohols to ketones or aldehydes.[6] Moreover, we have reported the aerobic photooxidation of phosphite esters to phosphate esters by using a diorganotelluride.[7] Even though organotellurium catalysts are valuable oxidation reagents, some limitations should be noted. For example, the resulting products usually require isolation and purification by chromatography, and it is generally necessary to use stoichiometric amounts of reagents, which hampers the recycling of the catalysts. Because of such synthetic, economic, and environmental concerns, it is evident that an improvement in this catalytic process is highly desirable.

To improve this catalytic process, we decided to immobilize the organotelluride catalysts onto an ionic liquid (IL) support. ILs have recently attracted substantial attention from scientists in various areas of research. Previously, we developed an easy-to-use and reusable reaction system by exploiting the advantages of an IL,[8] and more recently we have developed an IL-supported organotelluride catalyst that we subsequently employed for the aerobic oxidation of thiols to disulfides under photosensitized conditions. On the basis of that work, we concluded that this system, which provides the corresponding disulfides in good yields and circumvents the need for column chromatography, might be reusable and would therefore lower the environmental impact of this reaction.[9] A shortcoming of this system was that the IL-supported organotelluride catalyst could not be used for the oxidation of phosphite esters. Here, we describe the synthesis of a modified IL-supported bulky diaryltelluride reagent, and its application in the photooxidation of phosphite esters to phosphate esters.

Initially, we focused on the synthesis of the IL-supported organotelluride catalyst **5**, as shown in Scheme 1. The structure of this complex was confirmed by the ^{1}H and ^{13}C NMR spectroscopy. Coupling of 1,2-bis(2,4,6-triisopropylphenyl)ditellane with [4-(hydroxymethyl)phenyl]boronic acid (**1**) gave {4-[(2,4,6-triisopropylphenyl)tellanyl]phenyl}methanol (**2**). Subsequently, this was converted into the halo compound **3** by treatment with thionyl chloride. The reaction between **3** and *N*-methylimidazole gave the imidazolium salt **4**. The stable hydrophobic IL-supported organotelluride **5** was obtained by ion exchange of **4** with KPF$_6$. **5** is soluble in ILs, and is insoluble in water and solvents of low polarity. Therefore, we had successfully obtained a hydrophobic IL-supported organotelluride catalyst **5**.

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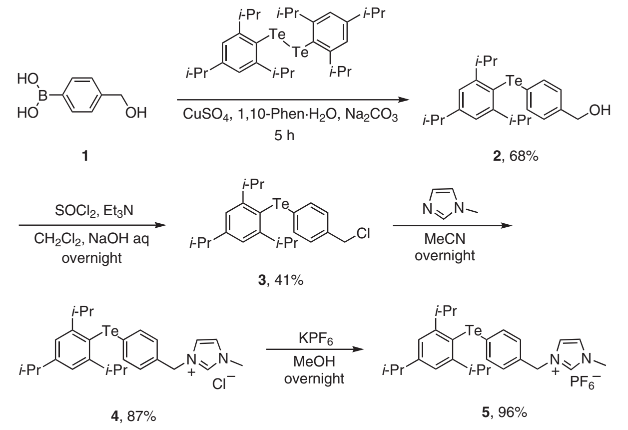


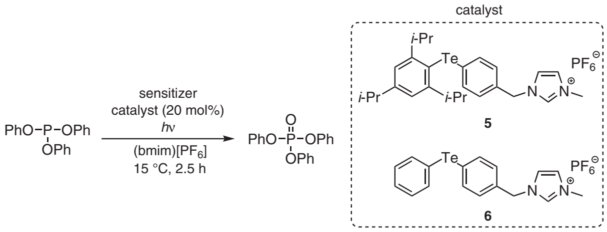
Scheme 1 Synthesis of the IL-supported diaryltelluride **5**

Next, we investigated the model oxidation reaction of triphenyl phosphite to triphenyl phosphate by using **5** under various reaction conditions. A solution of triphenyl phosphite, ditelluride **5**, and a photosensitizer [rose bengal (RB), methylene blue (MB), eosin Y, or tetraphenylphorphyrin (TPP)] was stirred for 2.5 hours in an open flask at 15 °C with irradiation by a white LED or halogen lamp. After the reaction, triphenyl phosphate was isolated by extraction into diethyl ether; the yields are summarized in Table 1. The catalytic activity of **5** was higher than that of the less-bulky IL-supported diphenyl telluride **6** (Table 1, entries 1 and 3). The synthesis of **6** was based on our previously developed protocol.[7] The use of RB as a photosensitizer afforded the best results in this reaction; other photosensitizers, especially TPP, afforded inferior results, probably because TPP is insoluble in ILs (entry 7). Furthermore, irradiation by LEDs gave a superior result to that produced by using a halogen lamp (entry 2). In other words, the best results for this model oxidation were obtained by using **5** and RB under irradiation from LEDs (entry 1). Note that the yield dropped significantly under a nitrogen atmosphere or with the exclusion of light (entries 8 and 9).

Next, we investigated the scope of the phosphite ester under the previously established optimal reaction conditions (Table 2). In all cases, the reactions proceeded rapidly and gave the expected phosphate esters in good to excellent yields (Table 2, entries 1–6). An exception was the oxidation of tris(4-methoxyphenyl) phosphite, which gave the corresponding phosphate ester in only 85% yield (entry 7).

A possible catalytic cycle is proposed in accordance with our previous communication (Scheme 2).[5] Triplet oxygen is converted into singlet oxygen by photosensitization under light irradiation. The telluride is then converted into the corresponding telluroxide and/or tellurone by singlet-oxygen oxidation. The telluroxide provides adduct **A** by attacking the phosphite ester. Subsequently, adduct **A** furnishes the telluride and the phosphate ester.

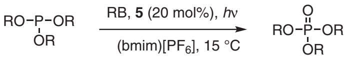
Table 1 Aerobic Oxidation of Triphenyl Phosphite Catalyzed by Organotellurium Catalysts **5** or **6**[a]



Entry	Catalyst	Sensitizer	Light source	Yield (%)
1	**5**	RB	LED[b]	97
2	**5**	RB	halogen lamp[c]	54
3	**6**	RB	LED	30
4	–	RB	LED	28
5	**5**	MB	LED	76
6	**5**	eosinY	LED	44
7	**5**	TPP	LED	12
8[d]	**5**	RB	–	17
9[e]	**5**	RB	LED	17

[a] Reaction conditions: $(PhO)_3P$ (0.25 mmol), catalyst (0.05 mmol), sensitizer (0.0125 mmol), (bmim)[PF_6] (5 mL), aerobic conditions, 15 °C, 2.5 h.
[b] 60 W LED.
[c] 500 W halogen lamp
[d] Shielded from light.
[e] Under N_2.

Table 2 Aerobic Oxidation of Various Phosphites Catalyzed by Organotellurium Catalyst **5**[a]



Entry	R	Time (h)	Yield (%)
1	Ph	2.5	99
2	i-Pr	1	93
3	2-Tol	2.5	95
4	4-Tol	2.5	99
5	4-FC_6H_4	2	quant
6	4-ClC_6H_4	2	97
7	4-$MeOC_6H_4$	2.5	85

[a] Reaction conditions: Phosphite (0.25 mmol), 5 (0.05 mmol), RB (0.0125 mmol), (bmim)[PF_6] (5 mL), LED (60 W), in air, 15 °C.

Finally, we examined the reusability of this reaction system in the oxidation of $(PhO)_3P$. When the oxidation of the phosphite was complete, the product was extracted with diethyl ether. The remaining (bmim)[PF_6] solution containing **5** and RB could be reused at least five times in subsequent reactions without any detectable deterioration in performance (Table 3).

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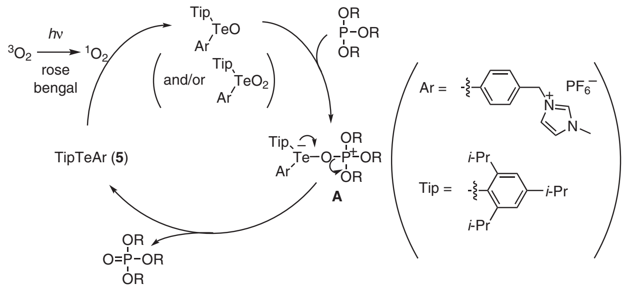
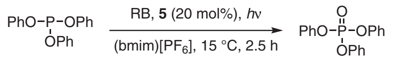


Scheme 2 Plausible reaction mechanism for the catalytic oxidation of phosphite esters

Table 3 Recycling of Catalyst 5[a]



Cycle	1	2	3	4	5
Yield (%)	99	quant	quant	quant	quant

[a] Reaction conditions: $(PhO)_3P$ (0.25 mmol), **5** (0.05 mmol), RB (0.0125 mmol), (bmim)[PF_6] (5 mL), LED (60 W), in air, 2.5 h, 15 °C.

In summary, we have developed a hydrophobic ionic-liquid-supported bulky diaryltelluride **5** and demonstrated its catalytic utility in the aerobic oxidation of phosphite esters.[10] This system exhibits a desirable catalytic performance and a low environmental footprint due to its ability to be recycled.

Supporting Information

Supporting Information for this article is available online at https://doi.org/10.1055/s-0040-1706068.

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(10) **Triphenyl Phosphate (Table 2, Entry 1); Typical Procedure**
A solution of $(PhO)_3P$ (0.0773 g, 0.250 mmol) in (bmim)[PF_6] (5 mL) containing **5** (0.0330 g, 0.0500 mmol) and rose bengal (0.0128 g, 0.0125 mmol) was vigorously stirred in an open flask and irradiated with a 60 W LED lamp for 2.5 h. The temperature was kept at about 15 °C by using an ice bath during the irradiation. The resulting mixture was extracted with Et_2O, and the solvent was then evaporated to give a pink solid; yield: 0.0803 g (99%); mp 44–47 °C.
^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.36 (t, J = 7.7, 6 H), 7.25–7.19 (m, 9 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 150.6, 150.5, 130.0, 125.7, 120.3, 120.2. ^{31}P NMR (202 MHz, $CDCl_3$): δ = –17.7. HRMS (APCI): m/z $[M + H]^+$ calcd for $C_{18}H_{16}O_4P$: 327.0781; found: 327.0743.

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