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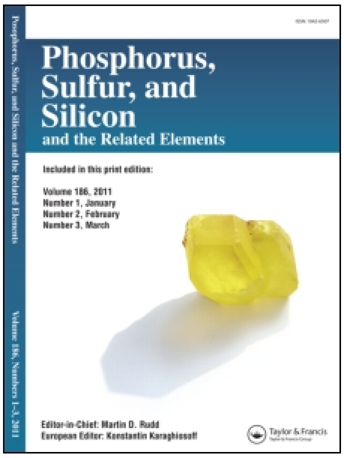

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Synthesis and Application of *O*-Xylylenebis(triphenylphosphonium Peroxymonosulfate) for Selective Oxidation of Benzylic Alcohols and Hydroquinones

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This article describes the oxidation of benzylic, allylic alcohols and hydroquinones under solvent-free conditions using o-*xylylenebis(triphenylphosphonium peroxymonosulfate), which has been prepared by mixing an aqueous solution of* o-*xylylenebis(triphenylphosphonium bromide) with oxone at room temperature.*

Keywords benzylic alcohols; hydroquinones; oxidation; *O*-Xylylenebis(triphenylphosphonium peroxymonosulfate); solvent-free

INTRODUCTION

Organic reactions were found to occur efficiently in the solid state. Organic solid state reactions are usually carried out by keeping a mixture of finely powdered reactant and reagent at room temperature. In some cases, these reactions are accelerated by heating, shaking, irradiation with ultrasound, or grinding of the reaction mixture using a mortar and pestle. Since the chemistry of solid state organic reactions has only a very short history, it is not easy to uniformly interpret such reactions. Theoretical treatments of solid state reactions have many problems because theory, which has been developed to describe the solution reaction, is not simply applicable to solid state reactions. On the other hand, heterogeneous reactions that are facilitated by supported reagents on various solid inorganic surfaces have received attention in

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recent years.[1–4] The advantage of these methods over conventional homogeneous reactions is that they provide greater selectivity, enhanced reaction rates, cleaner products, and manipulative simplicity.[5–9]

The oxidation of alcohols to the corresponding carbonyl compounds is a transformation that is fundamental to synthetic organic chemistry, and numerous reagents and methods have been developed to carry out this important reaction.[10–11]

O-Xylylenebis(triphenylphosphonium peroxymonosulfate) **1** was prepared readily from an aqueous solution of oxone and *o*-xylylenebis(triphenylphosphonium bromide) in a quantitative yield at room temperature. This compound is a white and stable solid material, which could be stored for months without losing its activity. The structure of this reagent was confirmed by spectral data accompanied by elemental analysis and titrimetric methods (Scheme 1).

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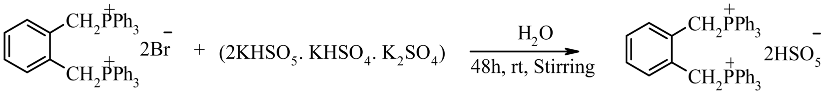

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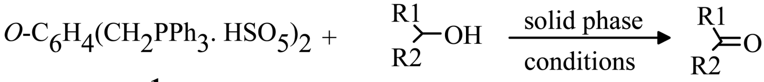
SCHEME 1

In connection with our recent work on the solvent free oxidations,[12] herein we report the oxidation of benzylic alcohols, allylic alcohols, and hydroquinones with **1** in the presence of Lewis acids under solvent free conditions as a new system which offers a simple, efficient, and selective oxidative method, for the preparation of carbonyl compounds. In this method, the reagent was carefully added to the substrate, and the mixture in a mortar was ground for the time specified in Table I until TLC analysis indicated a complete reaction. Most reactions are carried out at room temperature. In general, the oxidations were completed within 5–15 min. The effectiveness of various Lewis acids such as $AlCl_3$, $ZnCl_2$, $FeCl_3$, and $BiCl_3$ showed that $AlCl_3$ was the most effective catalyst for this purpose. The reaction in the presence of other Lewis acids proceeds with lower efficiency even with a higher (1–2) molar ratio of the oxidant.

The oxidation of alcohols with **1** in the presence of $AlCl_3$ proceeds well under solid phase conditions (Scheme 2).



1 **2** **3**

SCHEME 2

TABLE I Oxidation of Benzylic Alcohols and Hydroquinones with 1 at Room Temperature

Entry	R1	R2	Substrate/ Oxidant	Time (min)	Yield (%)[ab]
1	C_6H_5	H	1/1	3	98
2	2-ClC_6H_4	H	”	6	96
3	4-ClC_6H_4	H	”	6	96
4	4-MeOC_6H_4	H	”	6	95
5	3-MeOC_6H_4	H	”	15	80
6	2-MeC_6H_4	H	”	10	90
7	2-$NH_2C_6H_4$	H	”	5	90
8	2-BrC_6H_4	H	”	5	96
9	4-BrC_6H_4	H	”	5	98
10	3-$NO_2C_6H_4$	H	1/2	15	85
11	2-$NO_2C_6H_4$	H	”	15	70
12	C_6H_5	CH_2CH_3	2/1	5	98
13	C_6H_5	Me	”	5	95
14	C_6H_5	C_6H_5	”	10	92
15	$C_6H_5CH{=}CH$	H	1/2	15	80
16	$C_6H_5C{=}O$	C_6H_5	”	10	90[a]
17	$C_6H_5CH_2$	H	”	30	N.R
18	C_7H_{15}	H	”	”	”
19	Phenol	—	”	”	”
20	α-Naphthol	—	”	”	”
21	Hydroquinone	—	1/1	3	98
22	*tert*-Butyl hydroquinone	—	”	5	95

[a] Products were characterized by their physical constants, spectral characteristics (IR, ^1H NMR), and comparison with authentic samples.

[b] Yields are of pure isolated products.

RESULTS AND DISCUSSION

The results were shown in Table I. Primary and secondary benzylic alcohols are oxidized quantitatively in a short time (entries 1–9, and 12–14). However, aliphatic alcohols are unaffected even when using a higher molar ratio of an oxidant and a higher temperature (entries 17, 18).

Benzylic alcohols bearing strong electron-withdrawing groups on the aromatic ring need higher molar ratios of an oxidant and give lower yields (entries 10, 11). A noteworthy advantage of this reaction lies in its ability to the selective oxidation of benzylic and allylic alcohols in the presence of the other functional groups, such as a double bond. When we treated α, β-unsaturated alcohols with **1**, only the OH group was

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selectively oxidized to the corresponding carbonyl compounds, and the double bond remained intact (entry 15). α-Hydroxy ketone was oxidized to the corresponding diketone using 2 equivalents of the reagent **1** at 45°C (entry 16). Phenols and α-naphthol were unreactive towards this reagent even at a higher molar ratio of oxidant and higher temperature (entries 19, 20).

Hydroquinones were oxidized with one equivalent of this agent and gave excellent yields of the corresponding benzoquinones (entries 21, 22).

In order to evaluate the selectivity of this reagent, the competitive reactions shown in Eqs. (1)–(3) were carried out. When an equimolar amount of 2-phenylethyl alcohol and benzyl alcohol was treated with the reagent **1** in the presence of $AlCl_3$, only benzyl alcohol was selectively oxidized (Eq. **(1)**). Treatment of 4-methoxybenzyl alcohol with one mole ratio of reagent **1** in the presence of equimolar amounts of 2-nitrobenzyl alcohol led to the exclusive oxidation of 4-methoxybenzyl alcohol (Eq. (2)). Similarly, when we treated one equimolar amount of benzyl alcohol with reagent **1** in the presence of an equimolar amount of benzaldehydsemicarbazone, only the benzyl alcohol was selectively oxidized and semicarbazone remained unchanged (Eq. (3)). Interestingly, in the oxidation of alcohols, the overoxidation of products to the corresponding carboxylic acids was not observed at all.

$$\mathrm{PhCH_2CH_2OH + PhCH_2OH \xrightarrow[\text{AlCl}_3\text{,5 min}]{\mathbf{1}} \underset{\text{(unchanged)}}{PhCH_2CH_2OH} + \underset{95\%}{PhCHO}} \quad (1)$$

$$\mathrm{2\text{-}NO_2C_6H_4CH_2OH + 4\text{-}MeOC_6H_4CH_2OH \xrightarrow[\text{AlCl}_3\text{,5 min}]{\mathbf{1}} \underset{\text{(unchanged)}}{2\text{-}NO_2C_6H_4CH_2OH} + \underset{90\%}{4\text{-}MeOC_6H_4CHO}} \quad (2)$$

$$\mathrm{PhCH{=}NNHCONH_2 + PhCH_2OH \xrightarrow[\text{AlCl}_3\text{,5 min}]{\mathbf{1}} \underset{\text{(unchanged)}}{PhCH{=}NNHCONH_2} + \underset{90\%}{PhCHO}} \quad (3)$$

It has also been found that this reagent has certain advantages over oxidizing agents in terms of amounts of oxidant, short reaction times required, higher product yields, and especially milder conditions (Table II).

In summary, we report here the preparation of *o*-xylylenebis-(triphenylphosphonium peroxymonosulfate) **1** as a mild, inexpensive,

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TABLE II Oxidation of Alcohols by 1 in Comparison With Other Oxidants

Substrate	Reagent	Ratio of Oxidant: Substrate	Time	Conditions	Yield (%)	Ref.
$PhCH_2OH$	(1)[a]	1:1	4 min	Solvent-free, r.t.	98	—
p-$MeOC_6H_5$		1:1	5 min		98	
$PhCH_2OH$	4-APCC[b]	1.5:1	2 h	Support on silica-gel	97	15
p-$MeOC_6H_5$		1.5:1	1.5 h		100	
$PhCH_2OH$	MnO_2	12.2:1	48 h	Solvent-free, r.t.	77	16
p-$MeOC_6H_5$			48 h		83	
$PhCH_2OH$	PFC[c]	1:1	45 min	CH_2Cl_2, r.t.	90	17[a]
p-$MeOC_6H_5$		1:1	50 min		90	
$PhCH_2OH$	n-BTPPDC	1:1	45 min	$CHCl_3$, reflux	100	17[b]
p-$MeOC_6H_5$		1:1	45 min		95	

[a] *o*-Xylylenebis(triphenylphosphonium peroxymonosulfate).
[b] 4-Aminopyridinium chlorochromate.
[c] Pyridinium fluorochromate.

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and stable oxidizing agent. The reagent is soluble in acetonitrile and DMSO and is slightly soluble in carbon tetrachloride, ether, and hexane. This is an efficient, rapid, mild, and inexpensive oxidant for the oxidation of benzylic, allylic alcohols, and hydroquinones to the corresponding carbonyl compound under solvent-free conditions in the presence of a catalytic amount of $AlCl_3$. This method is superior to previously reported methods in terms of high yields, purity of products, facile workup, cheaper reagent, and shorter reaction times.

EXPERIMENTAL

All yields refer to isolated products after purification. Products were characterized by comparison with authentic samples (IR and ^{1}H-NMR spectrum, thin layer chromatography, m.p. and b.p.). All ^{1}HNMR were recorded at 90 MHz in CCl_4 relative to TMS, and IR spectra were recorded on a Shimadzu 435 IR spectrophotometer. Spectra of solids were carried out using KBr pellets. All reactions were carried out under solvent-free conditions.

Preparation of *O*-Xylylenebis(triphenylphosphonium Peroxymonosulfate) *1*

A solution of *o*-xylylenebis(triphenylphosphonium bromide)[13] (24.2 mmol, 20.7 g) in 100 mL of water was prepared, then oxone (48.4 mmol, 29.7 g) (2 $KHSO_5$. $KHSO_4$. K_2SO_4) in water (100 mL) was added dropwise to the above solution and stirred for 48 h at room temperature.

The resulting precipitate was filtered and washed with cooled distilled water (50 mL) and dried in a desiccator under vacuum over calcium chloride to afford a white powder (95%), which was decomposed at 203–205°C to a dark brown material. ^{1}HMR: δ 7.90–6.85 (m. 40 H), δ 4.7 (d. 4 H, CH_2P). The content of active oxidizing agent (HSO_5^-) was determined by the titrimetric method.[14] Anal. calcd. for $C_{44}H_{40}O_{10}P_2S_2$: C, 61.73; H, 4.65. Found: C, 61.8; H, 4.7.

General Procedure for Oxidation of Alcohols (2) and Hydroquinones with Reagent 1

A mixture of alcohols (**2**) (1 mmol) or hydroquinones (1 mmol), oxidizing agent **1** (1 mmol), and 0.1 molar ratio of $AlCl_3$ in a mortar was ground for the time specified in Table I. When TLC showed complete disappearance of alcohol, the mixture was extracted with CH_2Cl_2. Evaporation of the solvent gave the corresponding carbonyl compound (**3**). The product was purified by column chromatography on silica gel using a mixture of ethyl acetate and hexane as an eluent (10:90).

Competitive Oxidation: Typical Procedure

A mixture of benzyl alcohol (1 mmol), 2-phenylethyl alcohol (1 mmol), oxidizing agent **1** (1 mmol, 0.855 g), and 0.1 molar ratio of $AlCl_3$ was ground in a mortar. The mixture was ground until TLC showed complete disappearance of benzyl alcohol (5 min). The other competitive reactions see (Eqs. (1)–(3) were carried out in the same manner as above.

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