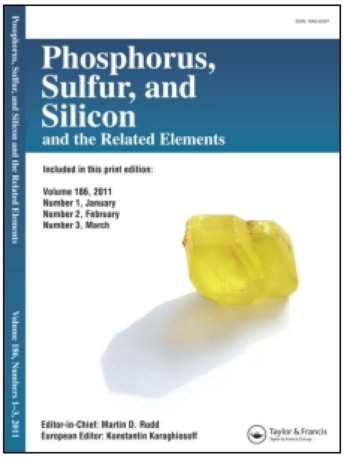

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OXIDATION OF ALCOHOLS WITH BENZYLTRIPHENYLPHOSPHONIUM CHLORATE UNDER NON-AQUEOUS CONDITIONS

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Oxidation of benzylic alcohols with benzyltriphenylphosphonium chlorate ($PhCH_2Ph_3P^+ClO_3^-$) 1 (BTPPC) in refluxing acetonitrile is reported. The oxidation in the presence of a catalytic amount of aluminum chloride enhances the rate.

Keywords: Alcohols; aluminum chloride; benzyltriphenylphosphonium chlorate; oxidation; sodium chlorate

INTRODUCTION

Oxidation of organic compounds in the absence of protic solvent is of importance. This subject has been under intensive investigation in recent years.[1–21] Along this line, we have introduced potentially oxidants in recent years.[25–27] In this article, we wish to report benzyltriphenylphosphonium chlorate ($PhCH_2Ph_3P^+ClO_3^-$) **1** as a mild and novel oxidizing reagent for oxidation of benzylic alcohols under nonaqueous conditions. This reagent is readily prepared by the dropwise addition of an aqueous solution of sodium chlorate to an aqueous solution of benzyltriphenylphosphonium chloride in quantitative yield at room temperature.

Results and Discussion

The oxidation of alcohols with $PhCH_2Ph_3P^+ClO_3^-$ **1** (BTPPC) in the presence catalytic amounts of Lewis acid proceeds under nonaqueous conditions. The effect of various solvents such as Et_2O, CH_2Cl_2, THF,

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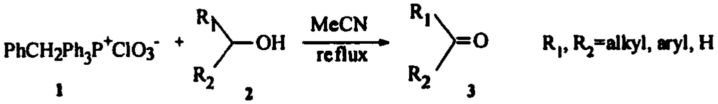
TABLE I Oxidation of Benzyl Alcohol with Reagent **1** in Different Refluxing Solvents[a,b]

Entry	Solvent	Time (min)	Yield (%)
1	Et_2O	120	30
2	THF	120	40
3	CH_2Cl_2	120	60
4	$CHCl_3$	120	70
5	CH_3CN	40	100

[a] Monitored by TLC analysis.
[b] Oxidant/Alcohol/$AlCl_3$ (1:1:0.2).

$CHCl_3$, and CH_3CN on the oxidation of benzyl alcohol with $PhCH_2Ph_3P^+ClO_3^-$ **1** in the presence of $AlCl_3$ was examined. TLC was used to monitor the rate of the oxidation. Only acetonitrile was a suitable solvent for this oxidation system (Table I).

Oxidation of benzyl alcohol to its corresponding aldehyde with reagent **1** in the presence of various Lewis acids such as $ZnCl_2$, $FeCl_3$, $BiCl_3$, and $AlCl_3$ were also examined in refluxing acetonitrile. Surprisingly, only $AlCl_3$ was shown to be an effective catalyst for this purpose (Table II). The reaction in the presence of $ZnCl_2$, $FeCl_3$, and $BiCl_3$ (0.5 mmol) proceeds with lower efficiency even with a higher molar ratio of the oxidant (1.5 mmol) in comparison with the amount of oxidant used in the presence of $AlCl_3$ (0.2 mmol). This could be the effect of hardness or high solubility of $AlCl_3$ in comparison with the other Lewis acids, which have been used in these experiments. Benzylic alcohols **2** are oxidized to the corresponding carbonyl compounds **3** in refluxing acetonitrile in the presence of aluminum chloride in good to excellent yields; benzoin was converted to benzil in high yield (Scheme 1). In comparison to benzylic alcohols, oxidation of aliphatic and allylic alcohols with this reagent does not occur at all. Therefore this reagent is not suitable for oxidizing aliphatic and allylic alcohols. Table III shows the experimental results.



SCHEME 1

A noteworthy advantage of this reagent lies in its ability to selectively oxidize benzylic alcohols in the presence of other oxidizable functional

TABLE II Oxidation of Benzyl Alcohol with Reagent **1** with Different Lewis Acids in Refluxing Acetonitrile[a,b]

Entry	Lewis acid	Time (min)	Yield (%)
1	$ZnCl_2$	120	50
2	$FeCl_3$	120	60
4	$BiCl_3$	80	65
3	$AlCl_3$	40	100

[a] Monitored by TLC analysis.

[b] Oxidant/Alcohol/Lewis acid (1:1:0.2).

groups. In order to evaluate the selectivity of reagent **1**, 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 reagent **1** (1 mmol), only benzyl alcohol was selectively oxidized (Eq. 1). Treatment of benzyl alcohol with reagent **1** (1 mmol) in the

TABLE III Oxidation of Alcohols **2** with Reagent **1** to Carbonyl Compounds **3** in Refluxing Acetonitrile in the Presence of Aluminum Chloride[a,b]

Compound	R_1	R_2	Time (hr)	Yield[c] (%)
2a	C_6H_5	H	0.40	100
2b	4-$NO_2C_6H_4$	H	15	100
2c	3,4-$(MeO)_2C_6H_3$	H	7	90
2d	4-PhC_6H_4	Me	5	100
2e	2-pyridyl	C_6H_5	17	80
2f	C_6H_5	Me	0.30	90
2g	4-$MeOC_6H_4$	H	16	75
2h	2-$MeOC_6H_4$	H	16	85
2i	C_6H_5	C_6H_5	0.15	100
2j	3-$MeOC_6H_4$	H	5	90
2k	4-ClC_6H_4	H	4	100
2l	2-ClC_6H_4	H	4	96
2m	C_6H_5	$C_6H_5CH_2$	0.50	98
2n	4-BrC_6H_4	Me	0.50	95
2o	4-ClC_6H_4	Me	1	100
2p	C_6H_5	C_6H_5CO	0.45	90
2q	2,3-$(MeO)_2C_6H_3$	H	4	100
2r[d]	$C_6H_5CH{=}CH$	C_6H_5	20	NR
2s[d]	$C_6H_5CH{=}CH$	Me	15	NR
2t[d]	4-$NO_2C_6H_4CH{=}CH$	H	15	NR
2u[d]	$C_6H_5CH{=}CH$	H	15	NR
2v[d]	$C_6H_5(CH_2)_2$	H	18	NR
2w[d]	$C_6H_5(CH_2)_3$	H	18	NR

[a] Confirmed by comparison with an authentic sample (IR, TLC, and NMR).[1–27]

[b] Oxidant/Alcohol/$AlCl_3$ (1:1:0.2).

[c] Yield of isolated pure product after chromatography or distillation.

[d] Oxidant/Alcohol/$AlCl_3$ (2:1:0.5).

presence of diphenylmethanol (1 mmol) led to exclusive oxidation of diphenylmethanol (Eq. 2). Interestingly, in the oxidation of alcohols the overoxidation of products to the corresponding carboxylic acids was not observed. When we treated benzyl alcohol (1 mmol) with reagent **1** in the presence of phenylmethyl sulfide (1 mmol), only the benzyl alcohol was selectively oxidized (Eq. 3).

$$\mathrm{PhCH_2CH_2OH + PhCH_2OH} \xrightarrow[\substack{\text{MeCN, reflux}\\ \text{4.5 hr}}]{\mathbf{1}} \underset{\text{(unchanged)}}{\mathrm{PhCH_2CH_2OH}} + \underset{(97\%)}{\mathrm{PhCHO}} \qquad \text{(Eq. 1)}$$

$$\mathrm{PhCH(OH)Ph + PhCH_2OH} \xrightarrow[\substack{\text{MeCN, reflux}\\ \text{4.5 hr}}]{\mathbf{1}} \underset{(95\%)}{\mathrm{PhCOPh}} + \underset{\text{(unchanged)}}{\mathrm{PhCH_2OH}} \qquad \text{(Eq. 2)}$$

$$\mathrm{PhSMe + PhCH_2OH} \xrightarrow[\substack{\text{MeCN, reflux}\\ \text{4.5 hr}}]{\mathbf{1}} \underset{\text{(unchanged)}}{\mathrm{PhSMe}} + \underset{(100\%)}{\mathrm{PhCHO}} \qquad \text{(Eq. 3)}$$

The reaction of secondary alcohols is faster than the reaction of primary alcohols. The functional groups such as NO_2 and MeO, decrease the rate of reaction. This could be the effect of producing complexes of these functional groups with $AlCl_3$ (Table III).

In order to evaluate the synergy between aluminum chloride and this reagent we tried several experiments. When we tried the reaction of benzyl alcohol with BTPPC **1** in refluxing acetonitrile without using any aluminum chloride, the reaction proceeds in 30% yield after 120 min. We also tried the oxidation of benzyl alcohol with $NaClO_3$ in refluxing acetonitrile as well as in a mixture of water and acetonitrile (50:50) without using any aluminum chloride. In the case of reaction with $NaClO_3$ in acetonitrile under refluxing conditions, the reaction does not proceed at all after 120 min, but in a mixture of water and acetonitrile (50:50) the corresponding aldehyde was obtained in 20% yield after 120 min refluxing. In another reaction we tried the reaction of benzyl alcohol with $NaClO_3$ in the presence of a catalytic amount of BTPPC **1** (0.2 mmol) in refluxing acetonitrile and the reaction proceeded in 10% yield after 3 h. We also investigated the use of $NaClO_3$ in the presence of aluminum chloride in refluxing acetonitrile and observed that the reaction does not complete after 2 h and that the corresponding aldehyde was obtained in 50% yield. The results of these experiments are summarized in Table IV.

This observation is in contrast to what is reported by us for 1-Benzyl-4-aza-1-azoniabicyclo[2.2.2]octane dichromate, which decomposes

TABLE IV Reaction of Benzyl Alcohol under Refluxing Conditions

Entry	Reagent	Solvent	Lewis acid	Time (min)	Yield[a] (%)
1	BTPPC	CH_3CN	—	120	30
2	$NaClO_3$	CH_3CN	—	120	NR
3	$NaClO_3$	CH_3CN-H_2O	—	120	20
4[b]	$NaClO_3$-BTPPC	CH_3CN	—	180	10
5[c]	$NaClO_3$	CH_3CN	$AlCl_3$	120	50
6[c]	BTPPC	CH_3CN	$AlCl_3$	24	100

[a] Monitored by TLC.
[b] BTPPC was used as catalytic amount (0.2 mmol).
[c] Oxidant/Alcohol/Lewis acid (1:1:0.2).

upon standing in solution.[14] The stability of this reagent in comparison with 1-Benzyl-4-aza-1-azoniabicyclo[2.2.2]octane dichromate is the reflection of the presence of the phosphonium cation in the reagent, which is more stable than ammonium cation.

In summary, we report here the preparation of benzyltriphenylphosphonium chlorate **1** as a mild, inexpensive, and stable oxidizing reagent. This oxidizing reagent is easily prepared from commercially available starting materials and could be stored for months without losing its activity. The reagent is soluble in acetonitrile, chloroform, and dichloromethane; it is slightly soluble in carbon tetrachloride, ether, and hexane. This compound is an efficient and novel reagent for oxidation of benzylic alcohols to the corresponding carbonyl compounds under nonaqueous conditions in the presence of catalytic amounts of $AlCl_3$. The reactivity of secondary alcohols with this oxidizing agent is higher than primary alcohols.

Experimental

General

All yields refer to isolated products after purification by column chromatography or distillation in vacuum. Products were characterized by comparison with authentic samples (IR and ^{1}H-NMR spectrum, TLC, melting and boiling point).[1–27] All ^{1}H-NMR spectra were recorded at 90 or 500 MHz in CCl_4 and $CDCl_3$ relative to TMS (0.00 ppm), and IR spectra were recorded on Shimadzu 435 IR spectrophotometer. All reactions were carried out in acetonitrile under reflux conditions. The Tarbiat Modarres University, Tehran, I.R. Iran performed elemental analysis.

Preparation of Benzyltriphenylphosphonium Chlorate 1 (BTPPC)

A solution of benzyltriphenylphosphonium chloride (19.0 g, 49 mmol) in 100 ml of water was prepared, then $NaClO_3$ (5.22 g, 49 mmol) in water (100 ml) was added dropwise to the above solution and stirred for 1 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 (19.25 g, 90% yield), which decomposed at 181–182°C to a dark-brown material. ^{1}H-NMR: δ 7.93–6.87 (m, 20 H), 4.7(d, J = 25.6 Hz, $\underline{CH2}$-P). ^{13}C-NMR: δ 135.28, 135.25, 134.32, 134.24, 131.07, 131.03, 130.19, 130.09, 128.99, 128.97, 128.69, 128.66, 127.45, 127.43, 118.01, 117.36, 29.68 (d, J = 193 Hz, $\underline{C}$-P). IR (KBr): 1298, 1269, 1098, 1060, 700, 658, 590 cm^{-1}. Anal Calcd for $C_{25}H_{22}ClO_3P$: C, 68.73; H 5.04%. Found: C, 68.90; H, 5.20%.

Oxidation of Alcohols 2 to the Corresponding Carbonyl Compounds 3 with Reagent 1 in Refluxing Acetonitrile in the Presence of $AlCl_3$

In a round-bottomed flask, a solution of alcohol **2** (1 mmol) in CH_3CN (5 ml) was treated with $BnPh_3P^+ClO_3^-$(0.44 g, 1 mmol) and aluminum chloride (0.03 g, 0.2 mmol) and refluxed for 0.15–17 hs. TLC (cyclohexane/EtOAc, 8:2) was used to monitor the reaction progress. The reaction mixture was cooled to room temperature, the solid filtered off, and washed with CH_3CN (15 ml). The filtrates were evaporated on a rotary evaporator and the resulting crude material was purified by column chromatography on silica gel with an appropriate eluent or distillation in vacuum to afford pure carbonyl compounds in 75–100% yields (Table III).

Competitive Oxidation

Typical Procedure

Benzyl alcohol (1 mmol, 0.11 g) and diphenylmethanol (1 mmol, 0.19 g) were added to a solution of the oxidant **1** (1 mmol, 0.47 g) in acetonitrile (15 ml). The mixture was refluxed until TLC showed the complete disappearance of diphenylmethanol (4.5 h). The other competitive reactions for Eqs. 1 and 3 were carried out under similar conditions.

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