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# Iodination of Alcohols over Keggin-type Heteropoly Compounds: A Simple, Selective and Expedient Method for the Synthesis of Alkyl Iodides

**Ezzat Rafiee[a,b,*], Houri Mahdavi[a] and Mohammad Joshaghani[a,b]**

[a]*Faculty of Chemistry, Razi University, Kermanshah, 67149, Iran.*
[b]*Kermanshah Oil Refining Company, Kermanshah, Iran.*

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**ABSTRACT**

**Different catalysts derived from Keggin-type heteropoly compounds were prepared and their catalytic activities have been compared in the iodination of benzyl alcohol with KI under mild reaction conditions. A high catalytic activity was found over tungstophosphoric acid supported on silica and titania. The effect of catalyst loading, iodine source and the nature of substituents on the aromatic ring of benzyl alcohol were investigated. Finally, several competitive reactions were studied between structurally diverse alcohols. This protocol provides a mild and expedient way for the conversion of various alcohols to their corresponding alkyl iodides with high selectivity.**

**KEYWORDS**

**Keggin-type heteropoly compounds, supported catalyst, alcohols, alkyl iodides, potassium iodide.**

## 1. Introduction

Organic halides are indispensable intermediates in organic synthesis, and their transformations to useful compounds are well documented in the literature.[1] Alkyl iodides or bromides are widely used for ionic and radical carbon-carbon coupling reactions and also act as intermediates in substitution, elimination and rearrangement reactions.[2] They can be converted to nucleophilic organolithium compounds *via* halogen-lithium exchange reactions.[3] Among them, iodides are the most reactive halides and in some cases, alkyl iodides show unique reactivity.[4]

Various methods have been demonstrated for the iodination of alcohols such as $BF_3$-$Et_2O$/CsI,[5] $BF_3$-$Et_2O$/KI,[6] $SOCl_2$–benzotriazole/KI,[7] $CeCl_3{\cdot}7H_2O$/NaI,[8] $P_4/I_2$,[9] $ZrCl_4$/NaI,[10] $AlCl_3$/CsI,[11] silica sulphuric acid (SSA)/KI,[12] $Al(HSO_4)_3$/KI,[13] $Ph_3P/I_2$,[14] $PPh_3$/DDQ/$R_4N^+X^-$,[15] polymethylhydrosiloxane (PMHS)/$I_2$,[16] $SO_4^{2-}/ZrO_2$/NaI,[17] Amberlyst-15/NaI,[18] and $Ru(TMHD)_3$/NaI.[19] Although some of these methods have convenient protocols with good to high yields, the majority of these methods suffer from drawbacks such as the presence of hazardous and toxic $I_2$,[9,14,16] use of strong mineral acids,[12,13,17] unsatisfactory yields for some substrates,[5,6,11,12,16] high temperature,[10,13,19] and use of expensive or non-commercially available materials[7,14–16,19]. In addition, some of the Lewis acids are moisture sensitive and require special care in handling and storage. Hence, to overcome such problems, the introduction of new methods with higher efficiency, lower toxicity, easy handling and also using inexpensive and commercially available materials is much needed.

In order to achieve this goal, use of Keggin-type heteropoly compounds (HPCs) as catalyst is a preferred technique owing to their versatility and unique properties. These compounds are promising solid acids, redox and bifunctional catalysts under homogeneous as well as heterogeneous conditions.[20] They exhibit high activities and selectivities and allow for cleaner processing compared to conventional catalysts and hence they are regarded as green catalysts.[21–23] As a consequence of some unique properties (multifunctional character, homogeneous, heterogeneous, pseudo-liquid and phase-transfer catalysis) and favourable technological features (easy recovery and environmentally safer handling), a variety of synthetically useful transformations have been developed using HPCs as catalysts which are being commercialized.[24] But there is still a growing interest in widening application possibilities. The structure and composition of heteropoly acids (HPAs) play an important role in catalysis and their catalytic properties can be controlled in a systematic way by replacing protons or by substituting framework transition-metal atoms with different metals.[25] Herein we describe a comprehensive study on the catalytic activity of different Keggin-type HPCs in the synthesis of alkyl iodides.

* To whom correspondence should be addressed.
E-mail: ezzat_rafiee@yahoo.com / e.rafiei@razi.ac.ir

## 2. Experimental

### 2.1. General

$H_3PW_{12}O_{40}$ ($PW_{12}$), $H_3PMo_{12}O_{40}$ and $H_4SiW_{12}O_{40}$ hydrate from Aldrich, Merck and activated carbon, KSF and K10 montmorillonite were purchased from Fluka. Aerosil silica and titania from Degussa were used. $\gamma$-Alumina was obtained from Aldrich. [(*n*-Bu)$_4$N]Br, [(*tert*-Bu)$_4$N]Br, $Cs_2CO_3$, $TiCl_4$, $SnCl_4$, KCl, sodium molybdate, sodium tungstate and di-sodium hydrogen phosphate from Merck, sodium metavanadate and $Co(OAc)_2{\cdot}4H_2O$ from Aldrich and $SnCl_2$ and $ZnCl_2$ was used from Fluka. KI, NaI, $I_2$, $CH_3CN$ and various alcohols were purchased from Merck and Aldrich. Products were characterized by comparing of their spectral data with those of the authentic samples. IR spectra were recorded with KBr pellets using a Shimadzu 470 spectrophotometer. $^1$H NMR spectra were recorded on a Bruker Avance 200 MHz NMR spectrometer with $CDCl_3$ as the solvent and TMS as the internal standard.

### 2.2. Catalyst Preparation

The synthesis of $K_5CoW_{12}O_{40}$ starts with the preparation of sodium tungstodicobaltate from cobaltous acetate (2.5 g,

0.01 mol) and sodium tungstate (19.8 g, 0.06 mol) in acetic acid and water. The sodium salt is then converted to the potassium salt by treatment with potassium chloride. Finally, the cobalt(II) complex is oxidized to the cobalt(III) complex by potassium persulphate (10 g). Then, the crystals of $K_5CoW_{12}O_{40}$ were dried.

$H_{(3+x)}PMo_{(12-x)}V_xO_{40}$ ($x$ = 2–4) catalysts were prepared from stoichiometric mixtures of sodium metavanadate, $Na_2MoO_4{\cdot}2H_2O$ and $Na_2HPO_4$ in water. $H_5PMo_{10}V_2O_{40}$ synthesis according to the following procedure is presented as example: sodium metavanadate (24.4 g) was dissolved by boiling in 100 mL of water and then mixed with 7.1 g of $Na_2HPO_4$ in 100 mL of water. Then this solution was cooled, 5 mL of concentrated sulphuric acid was added, and the solution developed a red colour. An addition of 121.0 g of $Na_2MoO_4$ dissolved in 200 mL of water was then made. While the solution was vigorously stirred, 85 mL of concentrated sulphuric acid was added slowly, and the hot solution was allowed to cool to room temperature. $H_5PMo_{10}V_2O_{40}$ was then extracted with 500 mL of diethyl ether. Evaporation of the solvent afforded a crude product which dissolved in water, concentrated to first crystal formation, and then allowed to crystallize further. The large red crystals that formed were filtered, washed with water, and air-dried. This procedure adopted for the preparation of $H_6PMo_9V_3O_{40}$ and $H_7PMo_8V_4O_{40}$ catalysts are the same as the preparation of $H_5PMo_{10}V_2O_{40}$ except the addition of the calculated amount of sodium metavanadate, by decreasing the corresponding amount of molybdenum salt. Reaction of $TiCl_4$ with aqueous solutions of sodium tungstate and sodium dihydrogen phosphate at pH 8–8.6 form $Na_7Ti_2W_{10}PO_4$. This sodium salt is then converted to the potassium salt by treatment with potassium chloride.

The synthesis of $[(n\text{-}C_4H_9)_4N]_{(7-n)}PMo_2W_9(M^{n+}.H_2O)O_{39}$, ($M^{n+}$ = $Ti^{4+}$, $Sn^{2+}$, $Sn^{4+}$ and $Zn^{2+}$), starts with the synthesis of $\beta$-$Na_8HPW_9O_{34}$. To a solution of sodium tungstate (6.0 g in 75 mL of water), 1.5 mL of $H_3PO_4$ (14.7 M) and 11 mL of HOAc (17.4 M) were added, respectively. The white powder, $\beta$-$Na_8HPW_9O_{34}$, was precipitated. For the preparation of $\alpha$-$K_7PMo_2W_9O_{39}$, $\beta$-$Na_8HPW_9O_{34}$ (11.0 g) was added to the aqueous solution of $Na_2MoO_4$ (20 mL, 1.0 M) and HCl (15 mL, 1.0 M). Finally, $\alpha$-$K_7PMo_2W_9O_{39}$ was precipitated by addition of KCl to the solution. To a solution of $\alpha$-$K_7PMo_2W_9O_{39}$ (3.5 g, 1.2 mmol in 25 mL of water), the chloride salt of the corresponding metal was added in excess. After 2 h of stirring, tetrabutylammonium bromide was added until a powder of $[(n\text{-}C_4H_9)_4N]_{(7-n)}PMo_2W_9(M^{n+}.H_2O)O_{39}$ precipitated. The powder was filtered and dried in a vacuum desiccator. For the preparation of $[(tert\text{-}C_4H_9)_4N]_5PW_{11}Co(H_2O)O_{39}$, the pH of a solution containing sodium tungstate (0.2 mol) and $Na_2HPO_4$ (0.02 mol) in water (150 mL) was adjusted to 5.5. The solution was boiled and a concentrated solution of $Co(OAc)_2$ (0.02 mol) was added dropwise. The hot solution was filtered and treated with a concentrated solution of [(*tert*-Bu)$_4$N]Br until $[(tert\text{-}Bu)_4N]_4PW_{11}CoO_{39}$ was precipitated.

The acidic salts of $Cs_xH_{3-x}PW_{12}O_{40}$ were prepared by adding the required amount of aqueous cesium carbonate to aqueous solution of $PW_{12}$ with stirring. An appropriate amount of the aqueous solution of $Cs_2CO_3$ (0.10 M) was added dropwise to the aqueous solution of $PW_{12}$ (0.08 M) at room temperature with vigorous stirring. The Cs content was adjusted by the amount of $Cs_2CO_3$ solutions added. From the beginning of the addition of $Cs_2CO_3$, very fine particles (precipitates) were formed to make the solution milky. The precipitate obtained was dried in a rotary evaporator.

All of above catalysts were characterized and identified by comparing their spectral and analytical data with those of authentic samples.[26–31]

Supported $PW_{12}$ catalysts ($PW_{12}$/support) were prepared by the wet impregnation method. Silica-supported $PW_{12}$ ($PW_{12}/SiO_2$) catalysts were prepared by impregnating silica (3.0 g) with an aqueous solution of $PW_{12}$ (2.0 g in 20 mL water). The mixture was stirred overnight at room temperature, followed by drying using a rotary evaporator.

Titania-supported $PW_{12}$ ($PW_{12}/TiO_2$) catalysts were prepared by impregnating titania (5.0 g) with an aqueous solution of $PW_{12}$ (2.0 g in 25 mL water). The mixture was stirred overnight at room temperature, followed by drying using a rotary evaporator.

For preparation of the K 10-supported $PW_{12}$ ($PW_{12}$/K 10), K 10 montmorillonite was dried in an oven at 120 °C for 2 h prior to its use as a support. After drying, 5.0 g of K 10 was taken. To prepare a catalyst with 40 % loading of PW, 2.0 g of PW was dissolved in 4 mL of dry methanol. This solution was added dropwise to predried K 10 with constant stirring with a glass rod. Initially, with addition of PW solution, the clay was in the powdery form, but on further addition of PW solution, the clay turned to a paste form. The paste on further stirring for 10 min resulted in a free flowing powder. A similar procedure was followed for the synthesis of KSF-supported $PW_{12}$ ($PW_{12}$/KSF). A catalyst based on $PW_{12}$ supported on $\gamma$-$Al_2O_3$ ($PW_{12}/\gamma$-$Al_2O_3$) was also prepared. The solution of $PW_{12}$ was prepared by dissolving 2.0 g $PW_{12}$ in 25 mL of water and 25 mL of methanol. Then 5.0 g $\gamma$-$Al_2O_3$ was dropped into the above solution under vigorous stirring to be impregnated for 24 h.

For preparation of carbon-supported $PW_{12}$ ($PW_{12}$/C), carbon was first subjected to an acid and base treatment to remove impurities. This catalyst was prepared by the pore filling impregnation technique with a $PW_{12}$ solution. After the impregnation, the catalyst was dried at room temperature for 24 h, and calcined at 200 °C for 3 h.

### 2.3. Typical Procedure for the Conversion of Alcohols to Iodides

To a stirred suspension of alcohol (1 mmol) and KI (1.5 mmol) in $CH_3CN$ (4 mL), an appropriate amount of the catalyst (according to Fig. 1) was added and the resulting mixture was stirred at room temperature. Progress of the reaction was followed by TLC. After completion of reaction, the reaction mixture was diluted with ether and filtered. The organic layer was washed with an aqueous solution of $Na_2S_2O_3$ (15 %, 10 mL), then $H_2O$ (2 × 10 mL). The organic layer was dried over anhydrous $Na_2SO_4$. Evaporation of the solvent gave a residue which was purified by column chromatography over silica gel using n-hexane/ethyl acetate as an eluent to afforded pure alkyl iodides.

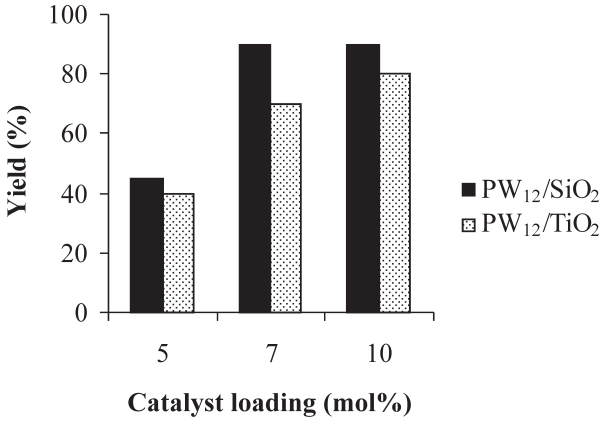
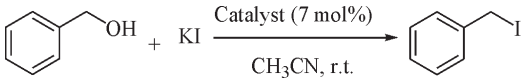



**Figure 1** Effect of catalyst loading in iodination of benzyl alcohol after four minutes.

**Table 1** Effect of different HPA-catalysts in iodination of benzyl alcohol.[a]




| Group | Catalyst | Time (min) | Yield (%)[b] |
|---|---|---|---|
| Single-addenda HPCs | $PW_{12}$ | 17 | 90 |
| | $H_3PMo_{12}O_{40}$ | 30 | 65 |
| | $H_4SiW_{12}O_{40}$ | 30 | 80 |
| HPC with paramagnetic ion | $K_5CoW_{12}O_{40}$ | 13 | 15 |
| Mixed-addenda HPCs | $H_5PMo_{10}V_2O_{40}$ | 30 | 15 |
| | $H_6PMo_9V_3O_{40}$ | 30 | 25 |
| | $H_7PMo_8V_4O_{40}$ | 45 | 15 |
| | $K_7PTi_2W_{10}O_{40}$ | 120 | 0 |
| Metal-substituted HPCs | $[(n\text{-Bu})_4N]_5PMo_2W_9(Sn^{2+}.H_2O)O_{39}$ | 120 | 0 |
| | $[(n\text{-Bu})_4N]_3PMo_2W_9(Sn^{4+}.H_2O)O_{39}$ | 120 | 0 |
| | $[(n\text{-Bu})_4N]_3PMo_2W_9(Ti^{4+}.H_2O)O_{39}$ | 120 | 0 |
| | $[(n\text{-Bu})_4N]_5PMo_2W_9(Zn^{2+}.H_2O)O_{39}$ | 120 | 0 |
| | $[(tert\text{-Bu})_4N]_4PW_{11}CoO_{39}$ | 13 | 15 |

[a] The molar ratio of alcohol: KI is 1:1.5. [b] Isolated yield.

### 2.4. Typical Procedure for the Competitive Reactions of Alcohols

An appropriate amount of the catalyst was added to a mixture of alcohols (1 mmol of each alcohol) and KI (1.5 mmol) in $CH_3CN$ (4 mL). Progress of the reactions was followed by TLC. Purification of products was similar to above procedure.

## 3. Results and Discussion

The most common precursors to alkyl halides are alcohols and their conversion into halides is a frequently encountered transformation in organic synthesis.[30] Thus, our studies have been focused on the conversion of structurally diverse alcohols as substrates to the corresponding iodides. Benzyl alcohol was selected as a model substrate for optimization of the reaction conditions.

Most of the publications in the literature used benzyl alcohol as a model substrate and we want to have a comparison of the results with those of (previously reported ones. In addition, benzyl alcohol showed a good yield thus, it makes easy to optimized reaction conditions. So, we first examined the catalytic performances of various HPCs on benzyl alcohol in acetonitrile at room temperature (Table 1). Single-addenda HPCs are the most effective catalysts in this reaction. The acid strength decreases when the $W^{+6}$ atom is replaced by $Mo^{+6}$ or when the central $P^{+5}$ atom is replaced by $Si^{+4}$.[31] Thus, the following order was expected to the acidity of HPA: $PW_{12} > H_4SiW_{12}O_{40} = H_3PMo_{12}O_{40}$.[20] This order of acidity agrees fairly well with the order of catalytic activity of these compounds in model reaction.

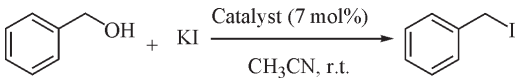
The extremely poor catalytic performance of $K_5CoW_{12}O_{40}$ seems to be due to its different catalytic mechanism. This catalyst is the most important example of a HPA, based on a d-transition-metal heteroatom ($Co^{+3}$), that is used as electron-transfer catalyst in some organic transformations.[32] It is apparently a perfect outer-sphere one-electron oxidant due to the presence of a sheath of chemically inert oxygen atoms, which protect the central ion from undesired inner-sphere substitution reactions.[32] The poor catalytic performance of $K_5CoW_{12}O_{40}$ indicated that this conversion is not proceed *via* electron-transfer mechanism.

Mixed-addenda HPCs showed poor yields or no catalytic activity in the model reaction. The replacement of $Mo^{+6}$ by $V^{+5}$ must result in an increase in the anion charge, the anion basicity increased and hence, the acidity and catalytic activity of the corresponding HPA decreased. Furthermore, $K_7PTi_2W_{10}O_{40}$ as an HPA-salt, showed no reactivity. This indicates that the catalytic activity is strongly dependent on the Brønsted acidity of the catalyst.

Metal substituted HPCs showed no catalytic activity in the model reaction. This behaviour can be explained by the high electron-acceptor character of these compounds which coordinate to the oxygen atom of alcohol to form an inert complexed species which cannot act as a leaving group. Based on these observations, $PW_{12}$ was selected as the suitable catalyst for more investigations.

In order to combine the favourable catalytic properties of $PW_{12}$ with the technical advantages related to the handling of a solid catalyst, catalytic performances of acidic cesium salts and $PW_{12}$/support catalysts were investigated in model reaction (Table 2). Acidic cesium salts were not efficient for this reaction

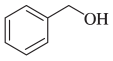
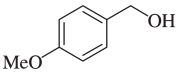
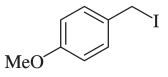
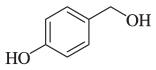
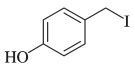
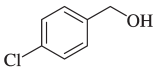
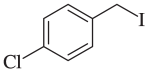
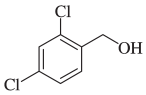
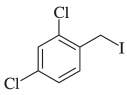
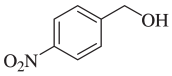
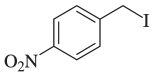
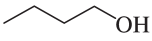
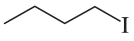
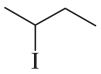
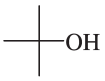
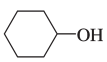
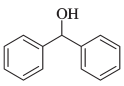
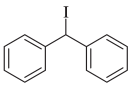
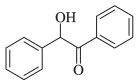
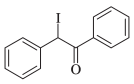
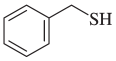
**Table 2** Effect of $PW_{12}$/support and acidic cesium salts in iodination of benzyl alcohol.[a]




| Entry | Catalyst | Time | Yield (%)[b] |
|---|---|---|---|
| 1 | $Cs_1H_2PW_{12}O_{40}$ | 90 min | 61 |
| 2 | $Cs_2H_1PW_{12}O_{40}$ | 90 min | 46 |
| 3 | $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ | 90 min | 39 |
| 4 | $SiO_2$ | 5 h | 10 |
| 5 | $TiO_2$ | 5 h | 16 |
| 6 | $\gamma$-$Al_2O_3$ | 5 h | 5 |
| 7 | Activated carbon | 5 h | 5 |
| 8 | K10 | 5 h | 8 |
| 9 | KSF | 5 h | 10 |
| 10 | 40 wt. % $PW_{12}/SiO_2$ | 4 min | 91 |
| 11 | 40 wt. % $PW_{12}/TiO_2$ | 3 min | 69 |
| 12 | 40 wt. % $PW_{12}/\gamma$-$Al_2O_3$ | 90 min | 17 |
| 13 | 40 wt. % $PW_{12}$/C | 90 min | 6 |
| 14 | 40 wt. % $PW_{12}$/K10 | 100 min | 28 |
| 15 | 40 wt. % $PW_{12}$/KSF | 100 min | 26 |

[a] The molar ratio of alcohol: KI is 1:1.5.
[b] Isolated yield.

**Table 3** Iodination of various alcohols using $PW_{12}/SiO_2$ and $PW_{12}/TiO_2$.[a]

| Entry | Substrate | Product[b] | Time (min)/Yield (%)[c] | |
|---|---|---|---|---|
| | | | $PW_{12}/SiO_2$ | $PW_{12}/TiO_2$ |
| 1 |  |  | 4/91 | 3/84 |
| 2 |  |  | 3/90 | 1/93 |
| 3 |  |  | 2/96 | 1/95 |
| 4 |  |  | 4/95 | 3/91 |
| 5 |  |  | 6/98 | 3/65 |
| 6 |  |  | 120/69 | 40/73 |
| 7 |  |  | 12/94 | 15/95 |
| 8 |  |  | 45/87 | 35/98 |
| 9 |  |  | 50/81 | 40/92 |
| 10 |  |  | 60/86 | 40/85 |
| 11 |  |  | 5/52 | 3/32 |
| 12 |  |  | 5/49 | 5/31 |
| 13 |  | - | 180/0 | 180/0 |

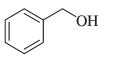
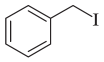
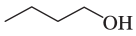
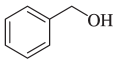
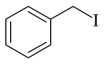
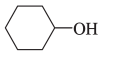
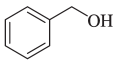
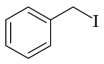
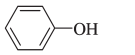
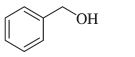
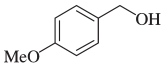
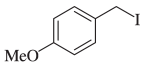
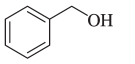
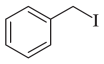
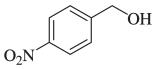
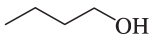
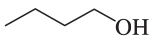
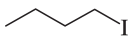
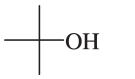
[a] The molar ratio of alcohol: KI is 1:1.5.
[b] All product showed physical and spectral data in accordance with their expected structures.
[c] Isolated yield.

and their catalytic activities decreased with increasing cesium content (Table 2, entries 1–3). This behaviour is in good agreement with the theoretical bulk Brønsted acidity of these catalysts. The reaction also runs on the $PW_{12}$/support and the bulk carriers (Table 2, entries 4–15). Only supported catalysts lead to promising results. Among them, $PW_{12}/SiO_2$ and $PW_{12}/TiO_2$ show the best results in terms of yield and reaction time (Table 2, entries 10, 11). Thus, further investigations were performed using different amounts of these catalysts in the model reaction.

Based on the results which have been shown in Fig. 1, 7 mol% of $PW_{12}/SiO_2$ and 10 mol% of $PW_{12}/TiO_2$ to benzyl alcohol were chosen as ideal amounts. Different iodine source, including KI, NaI and $I_2$ were used for the iodination of benzyl alcohol (Fig. 2). Electrophilic aromatic substitution may be obtained only when the iodide ($I^-$) reagent is oxidized into iodine in the presence of HPA. A remarkable low reaction rate strongly excludes the iodine formation *via* an electrophilic reaction.The highest yield of benzyl iodide was obtained by using KI. Thus, this reagent was used in further investigation.

The optimized reaction conditions were applied in iodination of several alcohols to elucidate the scope and limitations of this reaction (Table 3). First, we examined the effect of electron-donating and electron-withdrawing substituents on the aromatic rings of benzylic alcohols. The reaction is slightly accelerated by electron-donating groups (Table 3, entries 2, 3), and substitution of the electron-withdrawing groups on aromatic ring retards the transformation (Table 3, entries 4–6). The remarkable selectivity of this reaction allowed only the benzylic hydroxyl group to be iodinated without affecting the phenolic hydroxyl group present in the same molecule (Table 3, entry 3). Saturated alcohols required longer reaction times (Table 3, entries 7–10). It should be mentioned that oxidative-trimerization of aliphatic alcohols

**Table 4** Competitive reactions for selective iodination of different alcohols.[a]

| Entry | Substrate | Product[b] | Time (min)/Yield (%)[c] | |
|---|---|---|---|---|
| | | | $PW_{12}/SiO_2$ | $PW_{12}/TiO_2$ |
| 1 |  |  | 6/91 | 6/82 |
| |  | – | – | – |
| 2 |  |  | 4/92 | 5/83 |
| |  | – | – | – |
| 3 |  |  | 4/90 | 4/81 |
| |  | – | – | – |
| 4 |  | – | – | – |
| |  |  | 4/90 | 2/84 |
| 5 |  |  | 4/92 | 4/81 |
| |  | – | – | – |
| 6 |  |  | 12/88 | 15/89 |
| |  | – | – | – |
| 7 |  |  | 12/88 | 15/89 |
| |  | – | – | – |

[a] The molar ratio of alcohol: KI is 1:1.5.
[b] All product showed physical and spectral data in accordance with their expected structures.
[c] Isolated yield.

occurs in harder reaction conditions (high reaction temperature and long reaction time) and in iodide-free system. Thus, before oxidation, iodination of OH group occurs. Also, conversion of diphenylcarbinol and benzoin were carried out in low yields (Table 3, entries 11and 12). In the case of benzothiol, the conversion into the corresponding iodide was not carried out even after prolonged reaction time (Table 3, entry 13).

In order to evaluate the chemoselectivity of this method, several competitive reactions were studied between structurally diverse alcohols (Table 4). The reactions are highly selective for the conversion of benzyl alcohol in the presence of saturated alcohols (Table 4, entries 1, 2). Only the benzylic hydroxyl group undergoes iodination, while the phenolic hydroxyl group remains intact (Table 4, entry 3). Also, the reactions of 4-methoxybenzyl alcohol and 4-nitrobenzyl alcohol in the presence of benzyl alcohol have been studied. The reactions proceeded with high selectivity showing the importance of electronic effects upon these reactions (Table 4, entries 4, 5). Furthermore, selective

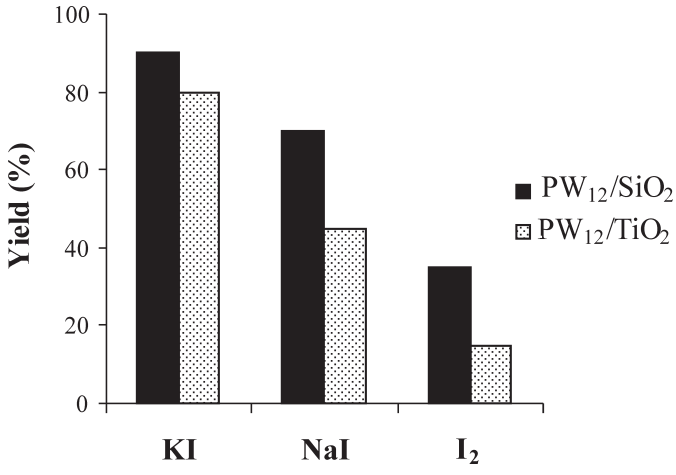
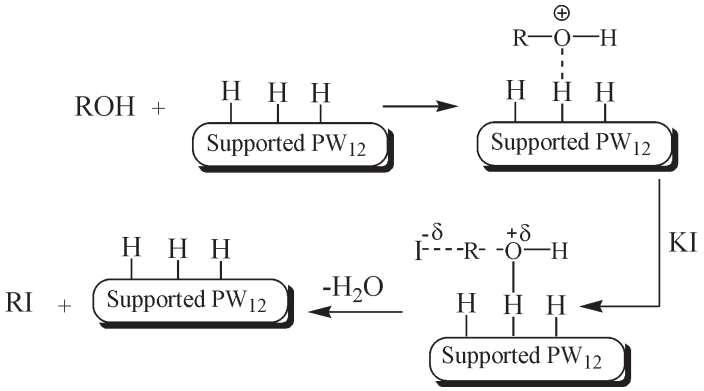



**Figure 2** Effect of iodine source in iodination of benzyl alcohol after four minutes.




**Scheme 1**
Reaction mechanism.

iodination of n-butyl alcohol was carried out in the presence of *sec*-butyl alcohol as well as *tert*-butyl alcohol (Table 4, entries 6, 7). Suggested mechanism is in Scheme 1, where the hydroxyl group of the alcohol is first protonated by the solid acid catalyst to form an excellent leaving group. The nucleophilic attack of the soft iodide ion on this cationic species, leads to the iodide product.

## 4. Conclusion

The conversion of benzyl alcohol into benzyl iodide has been investigated by a KI/HPC system in acetonitrile. The catalytic activity of HPCs is proportional to their Brønsted acidity and the highest catalytic activity was observed over $PW_{12}$ which possesses the highest acidity. Consequently, the reaction was performed in the presence of acidic cesium salts and $PW_{12}$/support. $PW_{12}/SiO_2$ and $PW_{12}/TiO_2$ have been employed as the best catalysts for the iodination of various alcohols in high to excellent yields. The comparative reactions indicate that this method is highly selective for the conversion of benzyl alcohol in the presence of other alcohols and also in the presence of 1° alcohols. The mild reaction condition, easy preparation, low toxicity of $PW_{12}$/support catalyst, and high to excellent yields of the products are the strong practical points of the present method. These advantages introduced HPCs as good catalysts for other organic synthesis.

## Acknowledgements

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