

## Research Article

# Tungstosilicic Acid: An Efficient and Ecofriendly Catalyst for the Conversion of Alcohols to Alkyl Iodides

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Treatment of a range of benzylic, allylic, and secondary aliphatic alcohols with potassium iodides in the presence of  $H_4SiW_{12}O_{40}$  affords the corresponding alkyl iodides in good to excellent yield with straightforward purification at room temperature in  $CH_3CN$ .

## 1. Introduction

Heteropolyacids (HPAs) and their salts are useful acid and oxidation catalysts for various reactions and there are already many practical applications. There are several advantages from using the HPA catalysts. One of the most interesting aspects may be the fact that they can be used in various kinds of reaction media or fields [1–3]. There are already several large-scale industrial processes utilizing HPA catalysts [4, 5]. The direct conversion of alcohols to alkyl iodides is a transformation that is widely utilized in organic synthesis [6]. Some alternative reagents reported for this purpose are  $PPh_3/I_2$ /imidazole [7],  $PPh_3/NIS$  [8],  $PPh_3/DEAD/MeI$  [9], and  $P(OPh)_3/MeI$  [10].

A common drawback of all these procedures is generating stoichiometric quantities of triphenyl phosphine oxide or diphenyl methylphosphonate, which can cause difficulties in product purification. Other methods avoid the use of phosphines, the use of HI [15], TMSI [16], *N,N*-diethylaniline:  $BF_3/I_2$  [17],  $TMSCl/NaI$  [18],  $P_2I_4$  [19],  $I_2$  [20], or of alkali metal iodides in conjunction with Lewis or Bronsted acids such as  $BF_3 \cdot OEt_2$  [21],  $CeCl_3$  [22],  $MsOH$  [23],  $Al(HSO_4)_3$  [24], sodium iodide over KSF-clay under microwave irradiation [25],  $KI/H_2SO_4$  supported on natural kaolinitic clay under microwave irradiation [26] cesium iodide/methanesulfonic acid [27], or  $MeSCH = NMe_2^+I^-$ /imidazole [28]. Also, the use of expensive and not easily

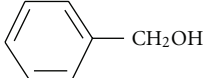
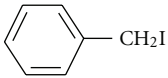
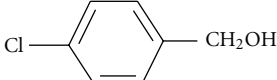
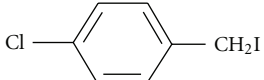
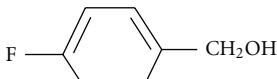
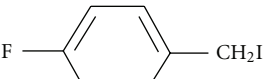
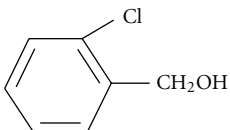
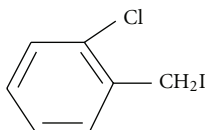
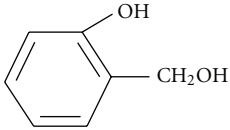
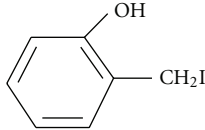
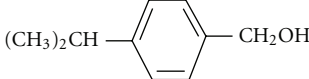
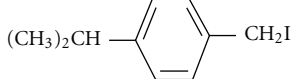
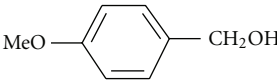
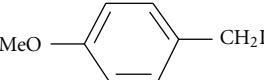
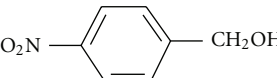
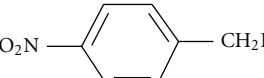
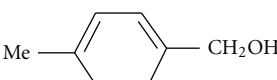
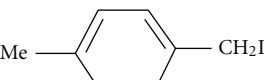
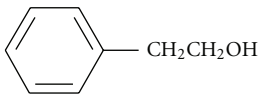
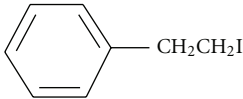
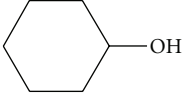
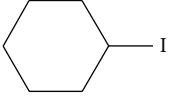
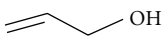
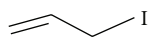
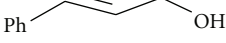
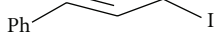
available reagents such as polymer-supported triphenylphosphine [29] or tris [4-(1*H*,1*H*-perfluorooctyloxyphenyl)] phosphine [30] is reported.

In this work, we describe a simple procedure for an efficient conversion of a wide range of allylic, secondary aliphatic, and benzylic alcohols to the corresponding iodides by treatment with the potassium iodide in the presence of  $H_4SiW_{12}O_{40}$  in  $CH_3CN$  at room temperature (Scheme 1).

## 2. Results and Discussion

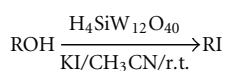
As shown in Table 1, a variety of benzylic, allylic, and secondary alcohols that were treated with potassium iodides in the presence of  $H_4SiW_{12}O_{40}$  affords the corresponding alkyl iodides in good to excellent yield at room temperature in  $CH_3CN$ . Primary benzylic alcohols (Table 1, entries 1–10) were easily converted to the corresponding benzyl iodides in good to excellent yields. Also, secondary aliphatic and benzylic alcohols (Table 1, entries 11–13) were converted to the corresponding iodides in good yields. No transformation took place when KI without  $H_4SiW_{12}O_{40}$  was heated under reflux for 12 h in acetonitrile. Furthermore, under the same reaction conditions, allylic alcohols formed allylic iodides in appropriate yields. It has been observed that the attacking of the iodide ion does not involve allylic rearrangement (Table 1, entries 14,15).

TABLE 1: Conversion of alcohols into alkyl iodides using  $H_4SiW_{12}O_{40}$  at room temperature.

Entry	Substrate	Product <sup>a</sup>	Time/h	Yield/% <sup>b</sup>
1			0.5	96
2			0.5	92
3			0.5	95
4			1	86
5			1	94
6			0.5	96
7			0.5	95
8			1	65
9			0.5	95
10			1	97
11	$(Ph)_2CHOH$	$(Ph)_2CHI$	3	80
12			1	60
13	$(CH_3CH_2CH_2CH_2)_2CHOH$	$(CH_3CH_2CH_2CH_2)_2CH_2I$	1	60
14			1	92
15			1	94

<sup>a</sup> All of the products were identified by comparing melting point and  $^1H$  NMR with those of authentic samples reported in the literature [11–14].

<sup>b</sup> Yields refer to isolated products.



SCHEME 1: Synthetic pathway for the conversion of alcohols to alkyl iodides.

To show the advantage of using heteropolyacid, some of our results compared with those reported in the literature.

As shown in Table 2, the iodination of benzyl alcohol with KI in the presence of  $H_4SiW_{12}O_{40}$  is simple, efficient, and higher yields of corresponding iodides are important features of this method.

In conclusion, the present research for the conversion of alcohols into iodides shows that our method may represent a valuable alternative to those reported in the literature. The superiority of this method is the ease of operation, the

TABLE 2: Comparison of H<sub>4</sub>SiW<sub>12</sub>O<sub>40</sub>/KI for the conversion of benzyl alcohol into iodide with other reagents.

Entry	Reagent	Reaction conditions	Time	Yield	Ref.
1	<i>N,N</i> -diethylaniline : BF <sub>3</sub> /I <sub>2</sub>	RT	12 h	86	[17]
2	Me <sub>3</sub> SiCl–NaI	RT	20 min	98	[18]
3	P <sub>2</sub> I <sub>4</sub> , CS <sub>2</sub>	RT	30 min	89	[19]
4	I <sub>2</sub>	Refluxing petroleum ether	1.5 h	56	[20]
5	NaI/BF <sub>3</sub> ·Et <sub>2</sub> O	RT	25 min	94	[21]
6	CeCl <sub>3</sub> ·7H <sub>2</sub> O/NaI	Refluxing acetonitrile	20 h	90	[22]
1	NaI, mont. KSF	MW	5 min	55	[25]
2	KI/H <sub>2</sub> SO <sub>4</sub> , kaolin clay	MW	5 min	92	[26]
9	CsI/MeSO <sub>3</sub> H	RT	15 min	95	[27]
10	H <sub>4</sub> SiW <sub>12</sub> O <sub>40</sub> /KI	RT	30 min	96	This work

simplicity of workup, and the environmental advantage that makes the process very useful.

### 3. Experimental

All chemicals were purchased from Merck. Melting points were recorded on an electro thermal melting point apparatus. The NMR spectra were recorded in CDCl<sub>3</sub> with TMS as an internal standard on a Bruker Avance DRX 250 MHz spectrometer. IR spectra were determined on a SP-1100, P-UV-Com instrument. Purity determination of the products was accomplished by TLC on silica gel poly gram SIL G/UV 254 plates. Products were identified by comparing IR and <sup>1</sup>H NMR spectra with those reported for authentic samples.

**3.1. General Procedure for the Conversion of Alcohols to Iodides.** To a mixture of H<sub>4</sub>SiW<sub>12</sub>O<sub>40</sub> (0.3 g), potassium iodide (2 mmol) in a flask were added acetonitrile (5 mL) and alcohol (1 mmol) at room temperature for 1–3 h. The reaction mixture was monitored by TLC in hexane/ethylacetate (4:1) as eluent. After completion of the reaction (TLC), ether (10 mL) was added and washed with aqueous saturated sodium hydrogen carbonate solution, followed by deiodination with sodium hydrogen sulfite. The resultant organic layer was extracted with ether (3 × 10 mL), and the combined extract dried over anhydrous sodium sulfate. The solvent was removed under reduced pressure to afford corresponding iodide in almost pure form. If necessary, products were purified by column chromatography (eluent, hexane-ethyl acetate, 95:5). The products were identified by IR and <sup>1</sup>H NMR.

#### 3.2. Spectral Data for Compounds.

**Benzyl Iodide (Table 1, entry 1).** <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ = 4.5 (s, 2H, ArCH<sub>2</sub>I), 7.4 (m, 5H, Ar–H).

**4-Chlorobenzyl Iodide (Table 1, entry 2).** <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ = 4.34 (s, 2H, ArCH<sub>2</sub>I), 7.23 (d, 2H, Ar–H), 7.32 (d, 2H, Ar–H).

**4-Flourobenzyl Iodide (Table 1, entry 3).** <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ = 4.44 (s, 2H, ArCH<sub>2</sub>I), 7.12 (d, 2H, Ar–H), 7.21 (d, 2H, Ar–H).

**2-Chlorobenzyl Iodide (Table 1, entry 4).** <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ = 4.2 (s, 2H, ArCH<sub>2</sub>I), 7.29 (m, 4H, Ar–H).

**2-Hydroxybenzyl Iodide (Table 1, entry 5).** <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ = 4.22 (s, 2H, ArCH<sub>2</sub>I), 6.83–7.09 (m, 4H, Ar–H).

**4-Isopropylbenzyl Iodide (Table 1, entry 6).** <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ = 1.31–1.33 (s, 6H, <sup>i</sup>Pr), 2.99 (m, 1H, –CH), 4.58 (s, 2H, ArCH<sub>2</sub>I), 7.27 (d, 2H, Ar–H), 7.40 (d, 2H, Ar–H).

**4-Methoxybenzyl Iodide (Table 1, entry 7).** <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ = 3.8 (s, 3H, OCH<sub>3</sub>), 3.9 (s, 2H, ArCH<sub>2</sub>I), 6.82 (d, 2H), 7.07 (d, 2H).

**4-Nitrobenzyl Iodide (Table 1, entry 8).** <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ = 4.48 (s, 2H, ArCH<sub>2</sub>I), 7.50 (d, 2H, Ar–H), 8.12 (d, 2H, Ar–H).

**4-Methylbenzyl Iodide (Table 1, entry 9).** <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ = 2.41 (s, 3H, CH<sub>3</sub>), 4.54 (s, 2H, ArCH<sub>2</sub>I), 7.21 (d, 2H, Ar–H), 7.36 (d, 2H, Ar–H).

**1-Iodo-2-phenyl-ethane (Table 1, entry 10).** <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ = 2.95 (t, 2H, CH<sub>2</sub>), 3.35 (t, 2H, CH<sub>2</sub>I), 7.00–7.12 (m, 5H, Ar–H).

**1,1-diphenyl Methyl Iodide (Table 1, entry 11).** <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ = 6.17 (s, 1H, ArCHI), 7.20–7.32 (m, 10H, Ar–H).

**Iodocyclohexane (Table 1, entry 12).** <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ = 0.85–0.99 (m, 4H), 1.4–1.75 (m, 6H), 3.89 (m, 1H, CHI).

**5-Iodononane (Table 1, entry 13).** <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ = 1.24–1.36 (m, 14H), 1.52–1.56 (m, 4H), 4.14 (m, 1H, CHI).

3-Iodo-1-propene (Table 1, entry 14).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta = 6.0\text{--}6.1$  (1H, m), 5.27–5.33 (1H, m), 5.09–5.12 (1H, m), 3.89 (2H, d,  $J = 7.5$  Hz,  $\text{CH}_2\text{I}$ ).

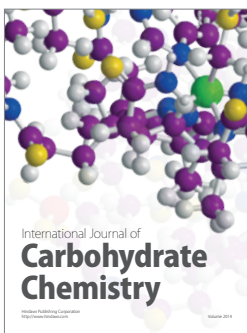
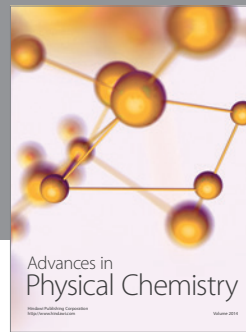
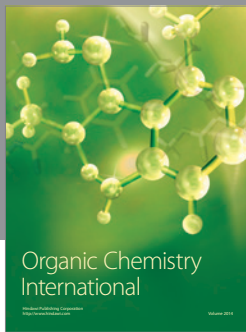
3-Iodopropenyl Benzene (Table 1, entry 15).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta = 3.4$  (d, 2H,  $\text{CH}_2\text{I}$ ), 6.6 (m, 1H, =CH), 6.8 (d, 1H, PhCH), 7.20 (d, 5H).

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