



Selective procedure for the conversion of alcohols into alkyl iodides with $\text{SO}_4^{2-}/\text{ZrO}_2$ and NaI at room temperature

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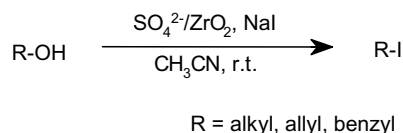
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Abstract

$\text{SO}_4^{2-}/\text{ZrO}_2$ was employed as a catalyst for the conversion of alcohols into the corresponding iodides using NaI in CH_3CN at room temperature. Present procedure is found to be selective for the conversion of benzylic alcohols in the presence of saturated alcohols into benzylic iodides. The catalyst was characterized by XRD, FTIR, elemental analysis, BET surface area and TG–DTA techniques. This protocol provides a mild and efficient way for the one pot conversion of structurally diverse alcohols to their corresponding alkyl iodides with high selectivity.



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Keywords: Benzylic alcohol; Iodination; Iodides; $\text{SO}_4^{2-}/\text{ZrO}_2$; Saturated alcohol

1. Introduction

Organic halides constitute a class of important intermediates, employed widely in organic synthesis [1,2]. The iodide or bromide subunit is an important structural motif involved in several carbon–carbon bond formation reactions. These compounds can also act as intermediates in variety of substitution, elimination and rearrangement reactions. The organic halides react with nucleophiles such as amines or alkoxides to give corresponding substituted products and can also be lithiated to introduce electrophiles via a halogen–lithium exchange reaction [3]. Prominent role of alkyl iodides is in the formation of car-

bon–carbon bonds by organometallic and free radical reactions as well as by nucleophilic substitutions [4]. Alkyl iodides are more expensive than other halides. As compared to other halides alkyl iodides are more reactive and in some cases these are the only reactive halides.

Several synthetic methods have been developed for the transformation of alcohols into iodides [5–11]. Bromotrimethylsilane–sodium iodide [12], chlorotrimethylsilane–sodium iodide [13], hexa-methyldisilazane–iodine [14], P_2I_4 in CS_2 [4], *N,N*-diethylanilineborane– I_2 [15], $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}/\text{NaI}$ [16], ZrCl_4/NaI [17], sodium iodide over KSF-clay under microwave irradiation [18] and Amberlyst 15/NaI [19] are some of the reported reagents. However, some of these methods suffer from drawbacks such as use of toxic and/or hazardous materials, expensive and commercially non-available reagents, low yields, long reaction times, and tedious work-up procedure. Hence to overcome such

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difficulties, mild and efficient methods which can promote the transformation of hydroxyl group into iodides are much needed.

We recently have reported several transition-metal based mesoporous silicates, mixed metal oxides and sulfated metal oxides, as catalysts for a variety of industrially important organic transformations [20–23]. Among sulfated metal oxides, $\text{SO}_4^{2-}/\text{ZrO}_2$ is a promising heterogeneous catalyst which exhibits a Hammett acid strength, $H_o \leq -16.04$. $\text{SO}_4^{2-}/\text{ZrO}_2$ exhibits excellent activity for a wide range of organic transformations, especially in the petroleum industry for alkylation, isomerization and cracking reactions [24–26]. Moreover this catalyst is safe, easy to handle and environmentally benign. We report herein, an exceedingly mild synthesis of iodides from alcohols using $\text{SO}_4^{2-}/\text{ZrO}_2$.

2. Experimental

2.1. Catalyst preparation

The catalyst was prepared as per reported procedure [27]. Zirconium (IV) hydroxide was prepared by adding 28 wt.% aqueous ammonia to an aqueous solution of $\text{ZrO} \cdot \text{Cl}_2 \cdot 8\text{H}_2\text{O}$ (0.3 M), until pH 8.4 was achieved with constant stirring. The precipitate was digested at 373 K over a waterbath for 1 h, washed with deionised water until a chloride free filtrate was obtained and finally was dried at 393 K for 24 h.

For sulfation, the 5 g of dry gel was introduced, at room temperature, into a 75 cm³ of a 1.0 N H_2SO_4 solution for 30 min under vigorous stirring and then filtered without washing, dried at 373 K and calcinated at 873 K for 4 h. The solid obtained after sulfation and calcination is designated as $\text{SO}_4^{2-}/\text{ZrO}_2$.

2.2. Catalyst characterization

The catalyst was characterized by XRD, FTIR, BET surface area, TG–DTA and elemental analysis techniques. XRD studies were performed with a conventional powder diffractometer (Philips 1050) using graphite monochromatized $\text{Cu K}\alpha$ radiation. FTIR spectra were recorded on Perkin-Elmer (Spectra 100). Surface area measurements were performed by nitrogen adsorption on a micromeritics (ASAP 2010) instrument at an adsorption temperature of 77 K. Thermal gravimetry (TG) and differential thermal analysis (DTA) studies were carried out between 273 and 1073 K, on a SETARAM TG–DTA A92 equipment with 32.5 mg of solid and a heating rate of 10 K min⁻¹ and an air flow of 20 cm³ min⁻¹.

2.3. General procedure for the conversion of alcohols to iodides

To a stirred suspension of alcohol (1 mmol) and NaI (0.150 g, 1 mmol) in CH_3CN (4 mL), $\text{SO}_4^{2-}/\text{ZrO}_2$

(1.25 mol%) was added and the resulting mixture was stirred at room temperature. After completion of the reaction Et_2O (10 mL) was added and the reaction mixture was washed with aqueous sat. NaHCO_3 . The resultant organic layer was extracted with Et_2O (3×10 mL) and the combined extract was dried over anhydrous Na_2SO_4 . The solvent was evaporated under reduced pressure to afford the iodides in almost pure form. Products were characterized by IR and ^1H NMR.

3. Results and discussion

3.1. Characterization of the catalyst

3.1.1. BET surface area and sulfur content

Surface area of zirconia was found to increase drastically after sulfate treatment. Untreated zirconia has surface area 27 m²/g, while zirconia modified by using 1.0 N H_2SO_4 has surface area 114 m²/g. This observation is in accordance with the literature [24]. Sulfur content of zirconia modified with 1.0 N H_2SO_4 was found to be 2 wt.%.

3.1.2. X-ray diffraction

Powder XRD was used to elucidate the crystalline phase of sulfated zirconia. It is generally observed that pure zirconia transforms into a monoclinic phase from a tetragonal phase above the calcination temperature of 873 K. But this transformation is prevented in $\text{SO}_4^{2-}/\text{ZrO}_2$ due to the sulfate treatment. Stabilization of the tetragonal crystalline phase, which is essential for catalytic behavior in sulfated zirconia, has been well explained in the literature [24,26]. The XRD patterns of ZrO_2 and $\text{SO}_4^{2-}/\text{ZrO}_2$ samples calcined at 873 K are shown in Fig. 1. The hydrous zirconia sample calcined at 873 K contains mixture of monoclinic and tetragonal phases. On the other hand, the sulfated sample exhibits prominent lines due to tetragonal phase indicating that the impregnated sulfate ions exert a strong influence on the phase modification of zirconia.

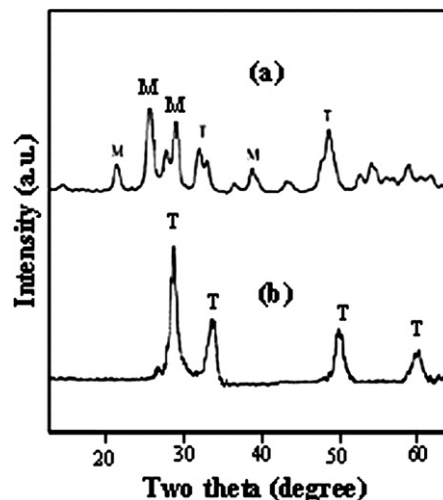


Fig. 1. XRD patterns of (a) ZrO_2 and (b) $\text{SO}_4^{2-}/\text{ZrO}_2$.

3.1.3. IR spectra of $\text{SO}_4^{2-}/\text{ZrO}_2$

The band at $1631\text{--}1642\text{ cm}^{-1}$ is attributed to O–H-bending of water molecules associated with the sulfate group [28]. It may thus be concluded that during the calcination at 873 K, condensation of the hydroxyl group of $\text{Zr}(\text{OH})_4$ occurs leading to a crystalline zirconia without any change of the nature of sulfate species. $\text{SO}_4^{2-}/\text{ZrO}_2$ exhibits strong bands at 998, 1066, 1153, 1218 cm^{-1} which shows bidentate sulfate ion coordinated to the metal [24]. These bands are absent in unsulfated ZrO_2 (Fig. 2).

3.1.4. TG–DTA analysis $\text{SO}_4^{2-}/\text{ZrO}_2$

TG–DTA studies of uncalcined and acid treated zirconium hydroxide are shown in Fig. 3. In case of zirconium hydroxide the first weight loss occurred at 373 K accompanied by an endothermic peak due to the loss of physically adsorbed water. The latter occurred continuously between 373 K and 723 K corresponding to the dehydroxylation process to form ZrO_2 . In case of uncalcined $\text{SO}_4^{2-}/\text{ZrO}_2$ the weight loss observed at 923 K can be attributed to the decomposition of sulfate species with the evolution of SO_2 .

3.2. Catalytic activity

The reaction was performed in different solvents. When benzyl alcohol with NaI catalyzed by $\text{SO}_4^{2-}/\text{ZrO}_2$ (1.25 mol%) reacted in various solvents such as CH_3CN , CH_3OH , Et_2O , EtOAc, CH_2Cl_2 and THF. We have found that reaction proceeds more rapidly and gives optimal yields in CH_3CN . As the reaction follows S_N mechanism, hence it is favored by polar aprotic solvents. The results are as shown in Table 1.

A variety of allylic, benzylic and saturated alcohols react satisfactorily under the chosen reaction conditions (Table 2, Scheme 1). For the optimization of the reaction conditions benzyl alcohol was chosen as a model substrate. When the reaction was carried out without catalyst in NaI no conversion took place, which implies that

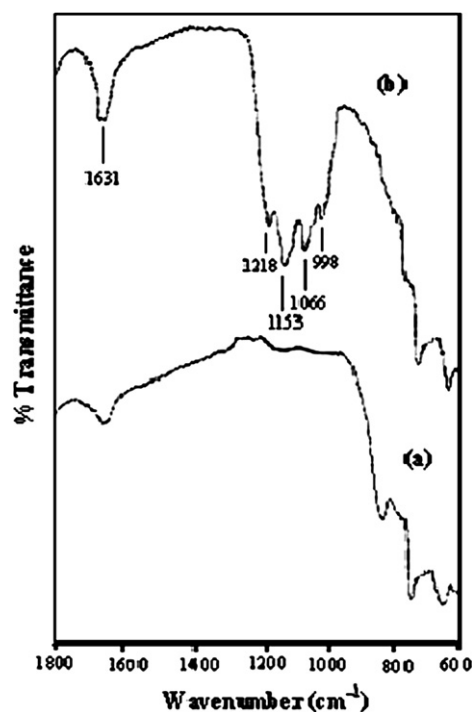


Fig. 2. FTIR spectra of (a) ZrO_2 and (b) $\text{SO}_4^{2-}/\text{ZrO}_2$.

Table 1

Effect of solvent on the iodination of benzyl alcohol with $\text{SO}_4^{2-}/\text{ZrO}_2$ –NaI system^a

Entry	Solvent	Time (h)	Yield (%)
1	None	3.0	12
2	THF	3.0	10
3	Et_2O	3.0	19
4	CH_2Cl_2	3.0	30
5	EtOAc	2.0	52
6	Acetone	1.0	82
7	CH_3CN	1.0	90
8	CH_3OH	1.0	70

^a All reactions were carried out at room temperature with benzyl alcohol (1 mmol), NaI (1 mmol), $\text{SO}_4^{2-}/\text{ZrO}_2$ (1.25 mol%) in CH_3CN solvent (4 ml).

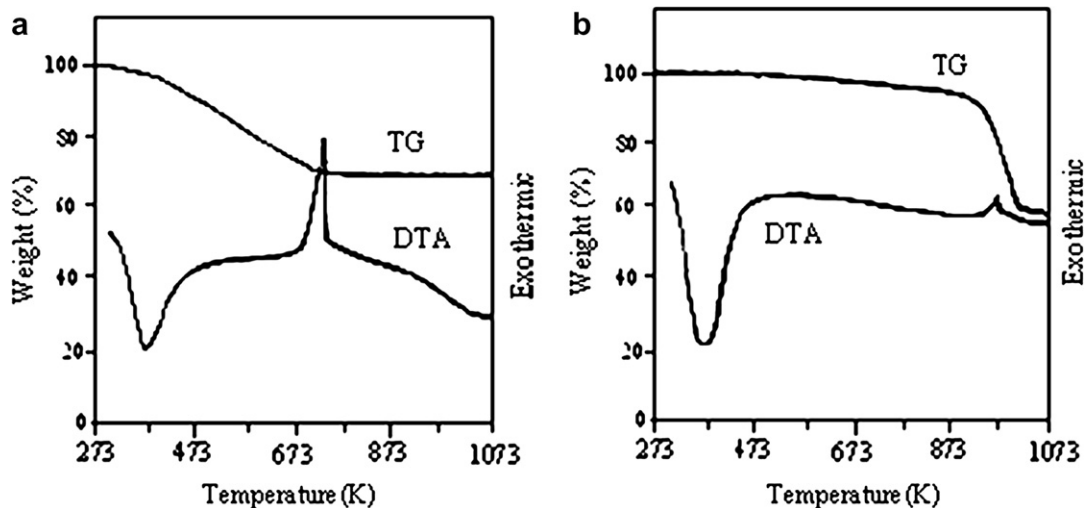


Fig. 3. TG–DTA profiles of (a) ZrO_2 and (b) $\text{SO}_4^{2-}/\text{ZrO}_2$.

Table 2
Conversion of alcohols into alkyl iodides using $\text{SO}_4^{2-}/\text{ZrO}_2$ and NaI in $\text{CH}_3\text{CN}^{\text{a,b,d}}$

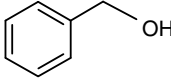
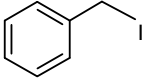
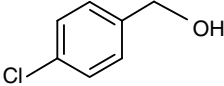
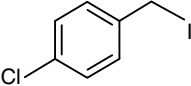
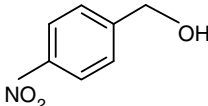
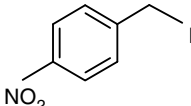
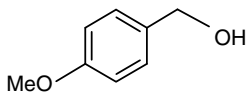
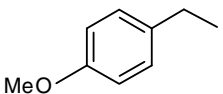
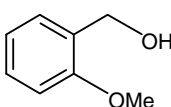
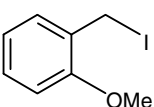
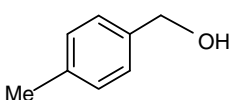
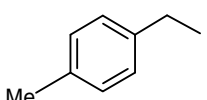
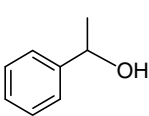
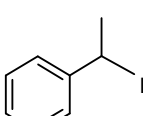
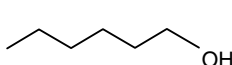
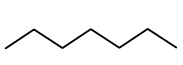
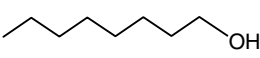
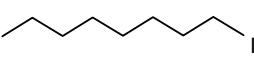
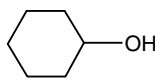
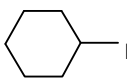
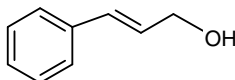
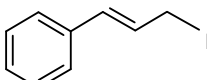
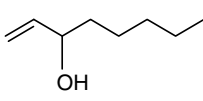
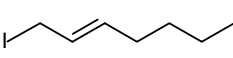
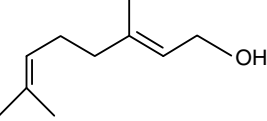
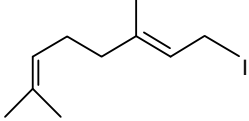
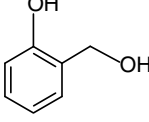
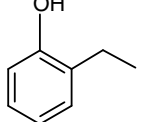
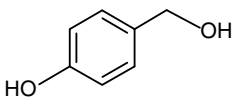
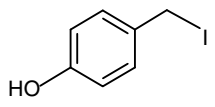
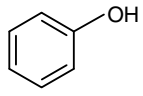
Entry	Substrate	Time (h)	Iodide ^c	Yield (%)
1		1.0		90
2		2.0		82
3		2.0		80
4		1.0		96
5		1.0		92
6		1.0		94
7		1.0		92
8		8		80
9		8		80
10		8		80
11		1.0		90
12		1.0		90
13		1.0		90
14		1.5		92

Table 2 (continued)

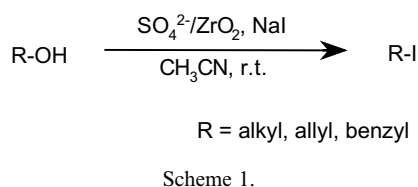
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16		10	n.r.	0

^a All reactions were carried out at room temperature with alcohol/NaI (1:1) molar ratio, $\text{SO}_4^{2-}/\text{ZrO}_2$ (1.25 mol%).

^b All products were characterized spectroscopically (IR, ^1H NMR).

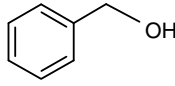
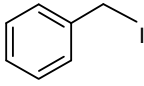
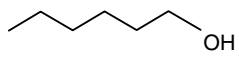
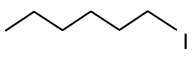
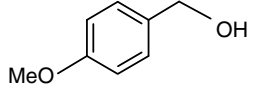
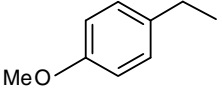
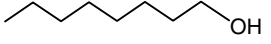
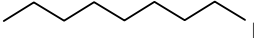
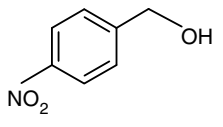
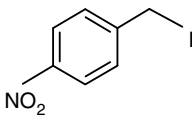
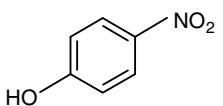
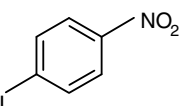
^c Yields refer to pure isolated products.

^d Purified by column chromatography.



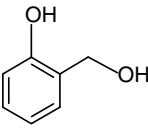
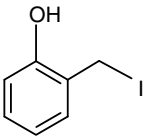
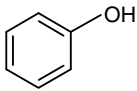
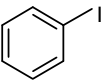
$\text{SO}_4^{2-}/\text{ZrO}_2$ plays prominent role in the reaction. We have carried out the reaction with both electron-donating and electron-withdrawing groups on the aryl ring. The substitution of the electron-withdrawing group on aryl ring retards the transformation (Table 2, entries 2 and 3). Furthermore, under the same conditions allylic alcohols form allylic

Table 3
Selective synthesis of benzyl iodides^{a,b}

Entry	Substrate	Time (h)	Iodide	Yield (%)
1		1		90
				0
2		1		96
				0
3		2		80
				0

(continued on next page)

Table 3 (continued)

Entry	Substrate	Time (h)	Iodide	Yield (%)
4		1.5		92
				0

^a All reactions were carried out at room temperature with substrate/NaI (1:1) molar ratio, $\text{SO}_4^{2-}/\text{ZrO}_2$ (1.25 mol%) in 4 ml of CH_3CN .

^b All products were characterized spectroscopically (IR, ^1H NMR) and by comparison with authentic samples [29,30].

Table 4

Comparison of the catalytic efficiency of $\text{SO}_4^{2-}/\text{ZrO}_2$ in the iodination of benzyl alcohol

Catalyst	Molar ratio (alcohol/NaI/catalyst)	Time (h)	Yield (%)	Reference
None	1:1:0	10 ^a	14	–
ZrO_2	1:1:1	10 ^a	20	–
$\text{SO}_4^{2-}/\text{ZrO}_2$	1:1:1	1 ^a	90	–
$\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$	1:1.2:1.5	20 ^c	90	[16]
ZrCl_4	1:1.5:0.5	10 ^{a,b}	95	[17]
Amberlyst 15	1:1	1 ^{a,d}	95	[19]

^a Reactions were performed at room temperature.

^b Time in minutes.

^c Reactions were conducted at reflux.

^d Catalyst amount used is 1 g.

iodides, which are not available commercially due to their rapid decomposition during storage. Allyl alcohol with a terminal double bond underwent iodination with an excellent yield accompanied by allylic rearrangement (Table 2, entry 12). Saturated alcohols required longer reaction times (Table 2, entries 8 and 9).

Selective iodination of benzylic alcohols was carried out in the presence of saturated alcohols as well as phenols (Table 3). Phenols do not react under the same conditions, while benzylic alcohols underwent iodination in the presence of saturated alcohols. Only alcoholic –OH group undergoes iodination, while phenolic –OH group remains intact. This shows the selectivity of the protocol (Table 2, entries 14 and 15).

3.3. Comparison of the catalytic efficiency

Catalytic efficiency of $\text{SO}_4^{2-}/\text{ZrO}_2$ for iodination of alcohols was compared with other solid acid catalysts reported for this reaction (Table 4).

3.4. Reusability study

Reusability of the $\text{SO}_4^{2-}/\text{ZrO}_2$ catalyst was tested by carrying out repeated runs of the reaction on the same batch of the catalyst. After each cycle the catalyst was filtered off, washed with acetone, dried at 393 K and then reused for successive cycles. It was observed that the activity of

Table 5

Study of reusability of $\text{SO}_4^{2-}/\text{ZrO}_2$ for the iodination of benzyl alcohol^a

Cycles	1	2	3	4	5
Yield (%)	90	88	88	87	82

^a All reactions were carried out at room temperature with benzyl alcohol/NaI (1:1) molar ratio, $\text{SO}_4^{2-}/\text{ZrO}_2$ (1.25 mol%) in 4 ml of CH_3CN .

$\text{SO}_4^{2-}/\text{ZrO}_2$ did not decrease appreciably even after five cycles (Table 5). No other reported procedures have mentioned the reusability of the catalyst used for the iodination of alcohols. Hence, this method is superior to the other reported methods.

4. Conclusion

$\text{SO}_4^{2-}/\text{ZrO}_2\text{--NaI}$ was found to be an effective system for the iodination of alcohols at room temperature. Selective iodination of benzylic alcohols can be achieved in the presence of saturated alcohols as well as phenols. Hence, the present procedure is a valuable alternative to the methods reported in the literature. Simplicity, easy work-up procedure is the features of this protocol.

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