

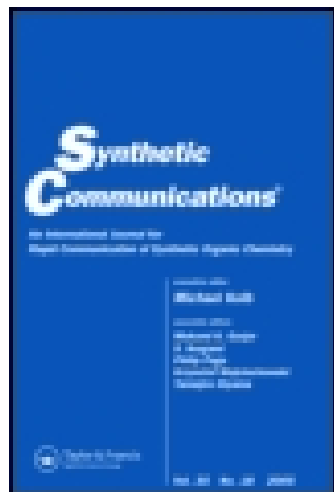
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Vikas N. Telvekar<sup>a</sup> & Omkar P. Herlekar<sup>a</sup>

<sup>a</sup> Department of Pharmaceutical Sciences and Technology, University Institute of Chemical Technology, Matunga, Mumbai, India

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## Mild and Recyclable Hypervalent Iodine System for Oxidation of Alcohols

Vikas N. Telvekar and Omkar P. Herlekar

Department of Pharmaceutical Sciences and Technology, University  
Institute of Chemical Technology, Matunga, Mumbai, India

**Abstract:** A simple and mild system for oxidation of primary and secondary alcohols to corresponding aldehydes and ketones has been developed using 4,4'-bis (dichloroiodo) biphenyl in combination with tetraethylammonium bromide (TEAB) at room temperature. Facile recovery and recyclability of the oxidant is reported.

**Keywords:** alcohols, 4,4'-bis(dichloroiodo)biphenyl, oxidation, recycle, tetraethylammonium bromide

### INTRODUCTION

Hypervalent iodine reagents and reagent systems found widespread applications in organic synthesis because of their selectivity and simplicity. Dess Martin periodinane (DMP) and iodoxybenzoic acid (IBX) emerged as reagents of choice for various synthetically useful oxidative transformations.<sup>[1,2]</sup> Major concerns with these reagents are that they are potentially explosive, they are hazardous to stock, and the generated iodine(III) species is usually not recycled or utilized.<sup>[3–5]</sup> Therefore, facile and efficient use of the readily available and relatively stable iodine(III) reagents in place of iodine(V) reagents has been long desired. There are few examples of the oxidation of alcohols using iodine(III) reagents.<sup>[6–8]</sup> Existing methods are limited to organic solvents and usually involve activation by use of Ru or Yb catalyst or 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO); also

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Address correspondence to Vikas N. Telvekar, Department of Pharmaceutical Sciences and Technology, University Institute of Chemical Technology, Matunga, Mumbai 400019, India. E-mail: vikastelvekar@rediffmail.com

reactions of these reagents with the organic substrate lead to iodobenzene as the by-product, which is difficult to recover and reuse because of its high volatility and solubility in organic solvents.

## RESULTS AND DISCUSSION

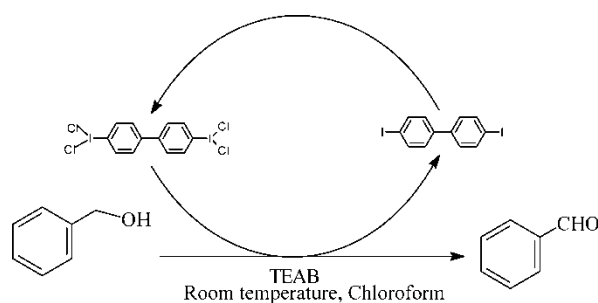
Our group has been working extensively on development of novel methodologies under mild reaction conditions using hypervalent iodine reagents.<sup>[9]</sup> Thus, we report our results on oxidation of primary and secondary alcohols using 4,4'-bis(dichloroiodo)biphenyl in the presence of tetraethylammonium bromide (TEAB) at room temperature.

For our initial study, benzyl alcohol was chosen as a substrate, and the reaction with 4,4'-bis(dichloroiodo)biphenyl in the presence of TEAB was performed (Scheme 1).

A variety of primary and secondary alcohols of aromatics, aliphatics, steroids, and carbohydrates were prepared as per the literature procedure and subjected to the reaction, and the results are presented in Table 1. The results clearly indicate that aromatic alcohols substituted with electron-donating groups such as methyl and methoxy undergo very fast oxidation (entries 2, 3, 8, 9); the reaction time is only 25 min and has good yields. On the other hand, if the aromatic ring is substituted with electron-withdrawing groups such as nitro and chloro, the reaction gives comparatively lower yields at slower reaction rates (entries 5, 6, 10, 11).

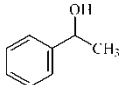
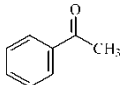
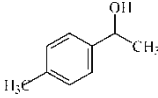
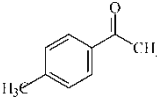
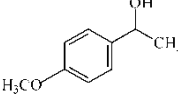
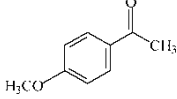
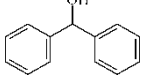
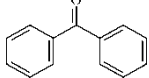
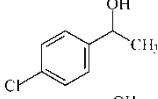
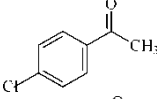
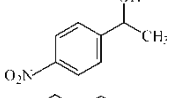
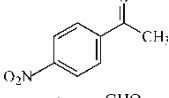
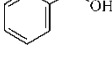

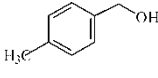
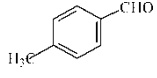
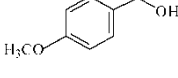
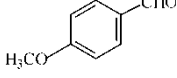
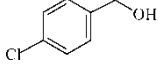
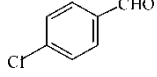
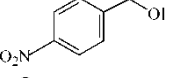
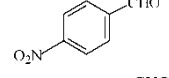
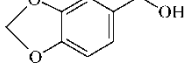
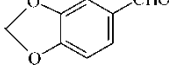
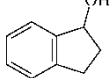
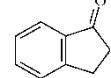
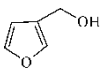

## GENERAL PROCEDURE

Benzyl alcohol (1.08 g, 10 mmol) was added to a stirred suspension of 4,4'-bis(dichloroiodo)biphenyl (3.1 g, 5.5 mmol) and TEAB (2.32 g, 11 mmol) in dry chloroform (10 ml) at room temperature. The reaction was monitored by thin-layer chromatography (TLC) (25 min; reaction mixture become clear). Reaction mixture was washed with water (2 × 25), followed



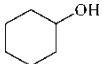
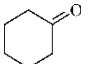
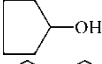
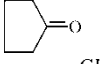



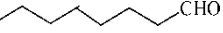
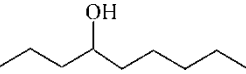
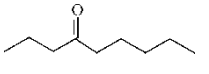
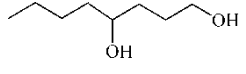
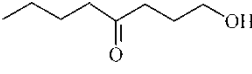
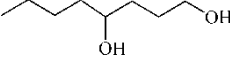
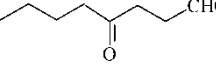
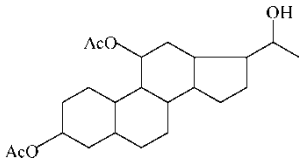
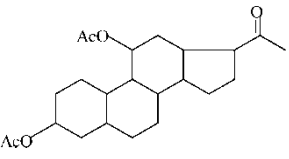
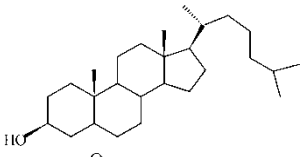
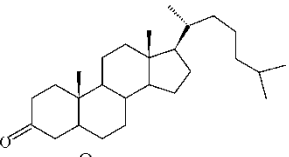
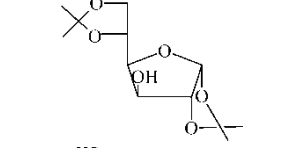
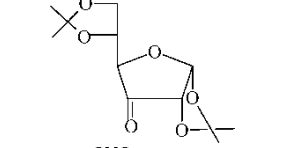
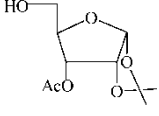
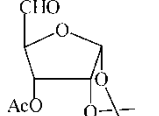
*Scheme 1.*

**Table 1.** Oxidation of alcohol using TEAB and 4,4'-bis(dichloroiodo)biphenyl<sup>a</sup>

Entry	Alcohol <sup>b</sup>	Product	Time (min)	Yield (%) <sup>d</sup>
1			20	93
2			25	94
3			20	94
4			20	95
5			35	90
6			35	90
7			25	95
8			25	93
9			20	95
10			35	90
11			40	90
12			45	91
13			25	93
14			30	93

(continued)

Table 1. Continued

Entry	Alcohol <sup>b</sup>	Product	Time (min)	Yield (%) <sup>d</sup>
15			25	90
16			20	92
17			45	90
18			40	90
19			25	92
20			25	93
21 <sup>c</sup>			45	90
22			30	25
23			25	30
24			30	25
25			45	35

<sup>a</sup>All reactions were carried out at room temperature using 1.0 equiv of substrate, 0.55 equiv of 4,4'-bis(dichloroiodo)biphenyl and 1.1 equiv of TEAB in dry dichloroform.

<sup>b</sup>Starting compounds were prepared by standard literature procedure and confirmed by reported data.

<sup>c</sup>1.0 equiv of substrate, 1.2 equiv of 4,4'-bis(dichloroiodo)biphenyl and 2.3 equiv of TEAB used.

<sup>d</sup>Isolated yields after column chromatography and structure confirmed by IR and <sup>1</sup>H NMR.

successively with 10% sodium bicarbonate (2 × 15 ml), 10% aqueous sodium bisulfite solution (2 × 15 ml), and finally with water (2 × 10 ml). The chloroform layer was separated, dried over sodium sulfate, and concentrated in vacuum, and the resultant residue was treated with hexane (25 ml). The precipitation of 4,4'-diiodobiphenyl was filtered and washed with hexane. The filtrate was dried over sodium sulfate and concentrated. The residue obtained was further purified by silica-gel column chromatography (10% EtOAc–hexane) to afford benzylaldehyde.

### Regeneration of 4,4'-bis(Dichloroiodo)Biphenyl

Isolated 4,4'-diiodo biphenyl from the reaction mixture was recrystallized and dissolved in chloroform, and excess of chlorine was bubbled through the solution for 1 h at 10–15°C under stirring. 4,4'-bis(Dichloroiodo)biphenyl precipitate was filtered, washed with cold chloroform, and dried [mp 155°C (dec), lit.<sup>[10]</sup> mp 156°C (dec)].

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