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# Simple System for Cleavage of Alkene C–C Bond Using Aqueous Sodium Paraperiodate

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**Abstract:** A simple and mild method for direct conversion of alkenes to corresponding aldehydes has been developed using sodium paraperiodate  $(Na_3H_2IO_6)$  in water. The reagent was found to give excellent yields of corresponding aldehydes.

Keywords: Aldehyde, C-C double bond, sodium paraperiodate, water

# INTRODUCTION

There are few methods in the literature for cleavage of alkene carboncarbon bond to aldehyde. Various one-pot methods are available, including RuCl<sub>3</sub> · H<sub>2</sub>O, OsO<sub>4</sub>, clay in combination with oxidants such as NaIO<sub>4</sub>, and oxone.<sup>[1-3]</sup> Heterogeneous catalysts such as calcined heteropolyacids on an oxide support in the presence of H<sub>2</sub>O<sub>2</sub> have also been reported for cleavage.<sup>[4]</sup> A few cases in the literature report carbon-carbon double bond oxidation by O<sub>2</sub> over TiO<sub>2</sub>/SiO<sub>2</sub> and selective oxidation of styrenes under O<sub>2</sub> catalyzed by cobalt chloride as well as tert-butyl hydroperoxide used in combination with AuCl.<sup>[5-7]</sup>

Most of these methods are unsatisfactory because of their long reaction times, harsh reaction conditions, use of complex reagents, and

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sometimes tedious workup, which means that there is still scope for alternative reagent systems for cleavage of alkene carbon–carbon bond to aldehyde.

Hypervalent iodine has emerged as a reagent of choice for oxidation of a broad range of functionalities, mostly because of their environmentally friendly nature and high selectivity. Our group has been working extensively on the development of novel methodologies under mild reaction conditions using the various iodine reagents.<sup>[8,9]</sup> Sodium paraperiodate is commercially available as a white crystalline solid. Because of its insolubility in almost all organic solvents and even water, it has not been exploited until now.

## **RESULTS AND DISCUSSION**

While working on oxidation systems, we observed that this reagent can be used for direct cleavage of the alkene carbon–carbon bond to aldehydes. For our initial studies, styrene was reacted with sodium paraperiodate. A mixture of styrene (10 mmol), sodium paraperiodate (12 mmol) in water, and a few drops of conc. sulfuric acid was stirred at 70°C. The starting material was consumed within 3 h as indicated by thin-layer chromatography (TLC). After workup and purification by silica-gel column chromatography (hexane–EtOAc, 9:1), benzaldehyde was isolated in 82% yield (Scheme 1).

The reaction does not take place in the absence of sulfuric acid. Sodium paraperiodate is practically insoluble in water, but with a few drops of sulfuric acid it forms a clear solution.

Encouraged by these results, a variety of aromatic and aliphatic alkene compounds were subjected to the reaction conditions, and the results are presented in Table 1. It is clearly indicated that the aromatic alkene C–C bond was converted into corresponding aldehydes in 3–4 h with good yields (Table 1, entries 1–8), but in the case of aliphatic alkenes, the reaction does not take place even after a long time (Table 1, entries 9 and 10).



Scheme 1. Styrene to benzaldehyde using sodium paraperiodate.

No.	Substrate <sup>b</sup>	Product	Time (h)	Yield (%)
1		ОНН	3.0	82
2	H <sub>3</sub> C	Н <sub>3</sub> С	3.5	84
3	ci	CI H	3.5	87
4	H <sub>3</sub> CO	НаСО Н	4.0	83
5		ОНН	4.0	87
6	H <sub>3</sub> CO	нзсо Н	4.0	86
7	CH3	ОН	3.5	83
8		С	4.5	85
9	H <sub>3</sub> C	$\mathbf{NR}^{d}$	24	
10	H <sub>3</sub> C CH <sub>3</sub>	NR	24	—

Table 1. Cleavage of carbon-carbon double bond using aqueous Na<sub>3</sub>H<sub>2</sub>IO<sub>6</sub><sup>a</sup>

<sup>*a*</sup>Typically, Na<sub>3</sub>H<sub>2</sub>IO<sub>6</sub> (12 mmol) reacted with substrate (10 mmol) in water (25 mL) at 70°C.

<sup>b</sup>Starting compounds were prepared by standard literature procedures.

<sup>c</sup>Isolated yields after column chromatography and structure was confirmed by comparison of IR and <sup>1</sup>H NMR with those of authentic materials.

<sup>*d*</sup>NR: no reaction.

A wide range of functional groups was tolerated by this protocol, and in these reaction conditions methoxy, ether, and ester groups were stable. No deprotection was observed (Table 1, entries 4–6).

#### Cleavage of Alkene C-C Bond

In summary, a novel method has been developed for cleavage of the alkene C–C bond to corresponding aldehydes using sodium paraperiodate in water at 70°C. The method developed is mild, easy to workup, and gives good to excellent yields of aldehydes for aromatic substrates.

## **GENERAL PROCEDURE**

### Preparation of Benzaldehyde

A few drops of conc. sulfuric acid were added to a stirred suspension of sodium paraperiodate (12 mmol) in water (25 mL) until the solution became clear (five to seven drops required). In this solution, styrene (10 mmol) was added. The resultant mixture was stirred at 70°C until the starting material had been completely consumed (TLC). After the completion of the reaction, the reaction mixture was extracted with CHCl<sub>3</sub> (25 ml). This organic layer was washed successively with 10% aq. NaHCO<sub>3</sub> (2 × 15 mL), 10% aq. sodium bisulfite solution (2 × 15 mL), and H<sub>2</sub>O (2 × 20 mL), dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated in vacuo. The residue obtained was purified by silica-gel column chromatography (10% EtOAc–hexane) to afford pure aldehyde.

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