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Abstract: A simple and mild method in water for direct conversion of epoxides to corresponding aldehydes has been developed using sodium paraperiodate $(Na_3H_2IO_6)$. High yields of corresponding aldehydes were obtained.

Keywords: Aldehydes, epoxides, sodium paraperiodate

INTRODUCTION

There are few methods in literature for conversion of epoxides to aldehydes. One-pot methods available include the use of $RuCl_3 \cdot H_2O$ or OsO₄ in combination with oxidants such as NaIO₄, oxone, and NaOCl.^[1,2] A few cases in the literature have reported the reaction of periodic acid or metaperiodic acid with epoxides, resulting in the corresponding carbonyl compound.^[3] Activated iodosylbenzene monomer was used for the direct conversion of epoxides to aldehydes.^[4,5]

Most of these methods are unsatisfactory, because of their long reaction time, harsh reaction conditions, use of complex reagents, and sometimes tedious workup, which means that there is still scope for alternative reagent systems for direct conversion of epoxides to aldehydes.

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Hypervalent iodine has emerged as reagent of choice for oxidation of a broad range of functionalities, mostly because of its 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.^[6,7] Sodium paraperiodate is commercially available as white crystalline solid. Because of its insolubility in almost all organic solvents and even in water, it has not been exploited until now.

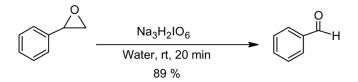
RESULTS AND DISCUSSION

While working on oxidation systems, we observed that this reagent can be used for direct oxidative cleavage of the epoxides rings to aldehydes. For our initial studies, styrene epoxide was reacted with sodium paraperiodate. A mixture of styrene epoxide (10 mmol), sodium paraperiodate (12 mmol) in water, and catalytically two to three drops of conc. sulphuric acid was stirred at room temperature. The starting material was consumed within 20 min as indicated by Thin-Layer Chromatography (TLC) analysis. After workup and purification by silica-gel column chromatography (hexane–EtOAc, 9:1), benzaldehyde was isolated in 89% yield (Scheme 1).

It is interesting that the reaction does not take place in the absence of sulphuric acid.

Encouraged by these results, a variety of aromatic and aliphatic epoxides were subjected to the reaction conditions, and the results are presented in Table 1. It is clearly indicated that aromatic epoxides were converted into corresponding aldehydes in 20–25 min in the good yields (Table 1, entries 1–6), but in the case of aliphatic aldehydes, slower reaction rates were observed (Table 1, entries 7 and 8). In the presence of bulkier groups, the reaction rates are still slower (Table 1, entries 9 and 10).

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



Scheme 1. Oxidative cleavage of styrene epoxide to benzaldehyde.

Oxidative Cleavage of Epoxides

| No. | Substrate ^b | Product | Time(min) | Yield(%) ^c |
|-----|---|-------------------|-----------|-----------------------|
| 1 | | O H | 20 | 89 |
| 2 | H ₃ C | H ₃ C | 25 | 87 |
| 3 | CI CI | CI H | 20 | 84 |
| 4 | H ₃ CO | H ₃ CO | 30 | 83 |
| 5 | | С С Н Н | 20 | 85 |
| 6 | H ₃ CO | H ₃ CO | 25 | 86 |
| 7 | $\sim \sim $ | ОЦН | 30 | 85 |
| 8 | ○ | H H H | 30 | 80 |
| 9 | CH3 | ОН | 50 | 83 |

Table 1. Synthesis of aldehydes from epoxides using aqueous $Na_3H_2IO_6{}^a$

(Continued)

| No. | Substrate ^b | Product | Time(min) | Yield(%) ^c |
|-----|------------------------|---------|-----------|-----------------------|
| 10 | | ОН | 120 | 82 |

Table 1. Continued

^{*a*}Typically, $Na_3H_2IO_6$ (12 mmol) reacted with epoxide (10 mmol) in water (25 mL) at room temperature.

^bStarting compounds were prepared by standard literature procedures.

^cIsolated yields after column chromatography and structure confirmed by comparison of IR and ¹H NMR with those of authentic materials.

In summary, a novel method has been developed for oxidation of epoxides to aldehydes using sodium paraperiodate in water at room temperature. The method developed is mild, easy to work up, has short reaction time, and gave good to excellent yields of aldehydes for both aliphatic as well as aromatic substrates.

GENERAL PROCEDURE

Preparation of Benzaldehyde

A few drops of conc. sulphuric acid (three to four drops required) were added to a stirred suspension of sodium paraperiodate (1.2 equiv) in water (25 mL). In this solution, epoxide (1.0 equiv) was added. The resultant mixture was stirred at it until the starting material had been completely consumed monitored by thin-layer chromatography, (TLC). The reaction mixture was extracted with CHCl₃ (25 ml), and this organic layer was washed successively with 10% aq. NaHCO₃ (2 × 15 mL), 10% aq. sodium bisulfite solution (2 × 15 mL), and H₂O (2 × 20 mL). The organic layer was dried over Na₂SO₄ and concentrated in vacuo. The residue obtained was purified by silica-gel column chromatography (10% EtOAc–hexane) to afford pure aldehydes.

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