

Epoxidation of cyclooctene and 1,5-cyclooctadiene by sodium perborate oxidation

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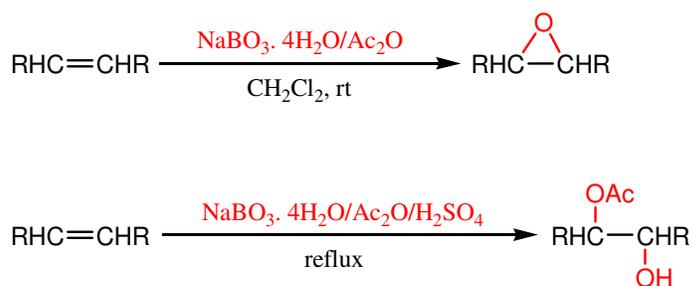
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Abstract: Sodium perborate oxidizes cyclooctene and 1,5-Cyclooctadiene to form the corresponding epoxides in good yields under mild conditions

Keywords: Cyclooctene; 1,5-Cyclooctadiene; epoxides; sodium perborate; sodium chloride.

1. Introduction

It was reported that sodium perborate ($\text{NaBO}_3 \cdot n\text{H}_2\text{O}$, $n=1-4$) is an excellent reagent for the oxidation of a wide class of organic compounds. It is an inexpensive, stable and easily handled oxidant and is often used in acetic acid or other carboxylic acids in synthesis.^{1,2} Sodium perborate tetrahydrate ($\text{NaBO}_3 \cdot 4\text{H}_2\text{O}$) oxidizes a wide range of acyclic and cyclic alkenes to form the corresponding epoxides and acetoxy alcohols³ (Scheme 1).

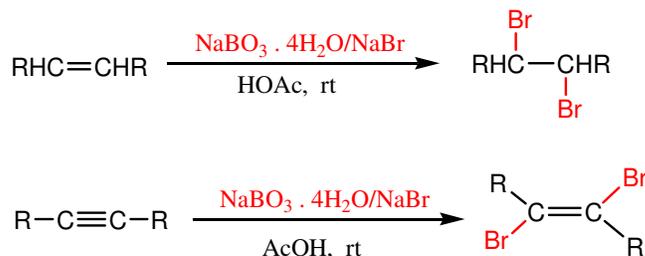


Scheme 1. Formation of epoxides and acetoxy alcohols by sodium perborate oxidation

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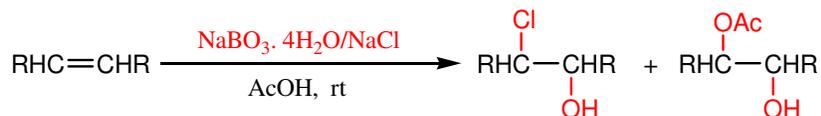
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A combination of sodium perborate and sodium bromide have been used for the bromination of alkenes⁴ and alkynes⁵ in acetic acid at room temperature and obtained the corresponding vicinal dibromo alkanes and *trans*-dibromo alkenes in good yields (Scheme 2). At high temperatures, bromination of alkenes results predominantly in the formation of solvolytic bromo derivatives, such as bromohydrins, bromo acetates, and acetoxy alcohols, by using this new bromination agent.⁶



Scheme 2. Bromination of alkenes and alkynes using sodium perborate and sodium bromide mixture

Recently, we have reported that sodium perborate oxidatively chlorinates a variety of alkenes with sodium chloride as the chlorine source in acetic acid at room temperature to form β -chlorohydrins and vicinal acetoxy alcohols as main products (Scheme 3).⁷

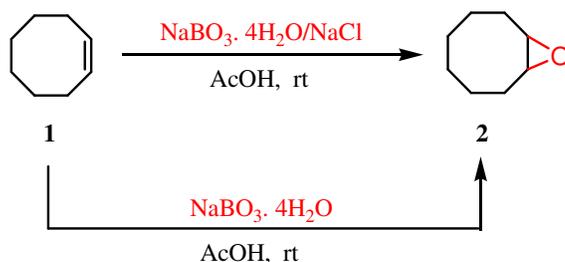


Scheme 3. Reaction of alkenes with sodium perborate and sodium chloride mixture

In the present work, we report that sodium perborate oxidation of cyclooctene and 1,5-cyclooctadiene in the presence or in the absence of sodium chloride results in the formation of the corresponding epoxides in good yields.

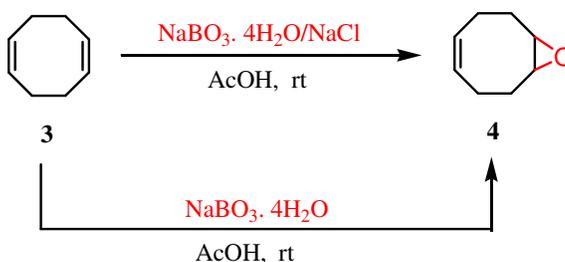
2. Results and Discussion

In a previous paper, we have shown that the reaction of cyclohexene, cycloheptene benzonorbornadiene and styrene with sodium perborate and sodium chloride mixture results in the formation of solvolytic products such as chlorohydrins, acetoxy alcohols, etc.⁷ Epoxides were not detected in any trace in these reactions. From the reaction of cyclooctene with sodium perborate we have obtained totally different results. When cyclooctene was treated with a mixture of sodium perborate and sodium chloride in glacial acetic acid at room temperature, 1,2-epoxycyclooctane **2** was formed as the sole product in a yield of 79% (Scheme 4). In order to reveal the effect of sodium chloride on epoxidation, the reaction was carried out in the absence of NaCl and again epoxycyclooctane **2** was obtained as the only oxidation product (Scheme 4). ¹H- and ¹³C NMR spectra of **2** were identical with those reported.⁸



Scheme 4. Reaction of cyclooctene with sodium perborate

Similar results were obtained from the reaction of 1,5-cyclooctadiene (3) with sodium perborate. 1,5-Cyclooctadiene was subjected to oxidation by using one or two equivalent of sodium perborate in glacial acetic acid at room temperature. In both cases, the known monoepoxide (4)^{9,10} was formed as the only oxidation product in the presence or in the absence of sodium chloride (Scheme 5).



Scheme 5. Reaction of 1,5-cyclooctadiene with sodium perborate

It was reported that most non-conjugated olefins react rather sluggishly with sodium perborate in acetic acid at room temperature below *ca.* 40 °C, and this process is of little use for epoxidation. At high temperatures and with prolonged reaction times oxidation can be effected to give mixtures consisting mainly of epoxides and vicinal acetoxy alcohols and the active oxidizing agent under these conditions is probably peracetic acid.² However, admixture of sodium perborate with acetic anhydride in dichloromethane is reported to result in generation of peroxybis(diacetoxy)borane, $(\text{AcO})_2\text{B-O-O-B}(\text{OAc})_2$, which reacts with alkenes to give epoxides in moderate to good yield (Scheme 1).³ By taking literature mentioned above into consideration, we assume that peracetic acid is responsible for the epoxidation of cyclooctene and 1,5-cyclooctadiene and the epoxide formation by sodium perborate oxidation is special for cyclooctane ring.

3. Conclusion

In conclusion, we have shown in the present study that sodium perborate oxidizes cyclooctene and 1,5-Cyclooctadiene to form the corresponding epoxides in good yields under mild conditions and the active oxidizing agent under the applied reaction conditions may be peracetic acid and also revealed that sodium chloride has no effect on the oxidation processes.

4. Experimental

General. ^1H and ^{13}C NMR spectra were recorded on 200 (50) and 400 (100)-MHz spectrometers. Column chromatography was performed on silica gel 60 (70-230 mesh, Merck). TLC was carried out on Merck 0.2 mm silica gel 60 F₂₅₄ analytical aluminum plates. NaCl was purchased commercially from Merck.

Reaction of Cyclooctene with Sodium Perborate and Sodium Chloride. 1.08 g (18.31 mmol) of sodium chloride was added to a mixture of sodium perborate (1.40 g, 9.09 mmol) and cyclooctene (1.00 g, 9.07 mmol) in glacial acetic acid (25 mL) and stirred at room temperature for 3 h. The mixture was then diluted with water (30 mL) and the aqueous solution was extracted with ether (3 x 60 mL), washed successively with saturated NaHCO₃ solution (3 x 30 mL) and water (3 x 30 mL) and dried over Na₂SO₄. After removal of the solvent, the residue was filtered on a short silica gel column (10.0 g) eluting with hexane-ethyl acetate (95:5) to give 0.90 g (79%) of epoxyoctene (**2**) as the sole product. Colorless oil; ^1H NMR (200 MHz, CDCl₃) δ 2.86-2.76 (m, 2H), 2.13-2.06 (m, 2H), 1.55-1.13 (m, 10H); ^{13}C NMR (50 MHz, CDCl₃) δ 57.18, 28.57, 28.30, 27.61.

Reaction of 1,5-Cyclooctadiene with Sodium Perborate and Sodium Chloride. The reaction was carried out at room temperature for 24 h as described above using 300 mg (2.77 mmol) of 1,5-Cyclooctadiene (**3**), 940 mg (6.06 mmol) of sodium perborate, 713 mg (12.19 mmol) of sodium chloride and 15 mL of glacial acetic acid and after work-up the residue was filtered on a short silica gel column (10.0 g) eluting with hexane-ethyl acetate (9:1) to give 210 mg (61%) of 5,6-epoxycyclooctene (**4**) as the sole product. Colorless oil; ^1H NMR (400 MHz, CDCl₃) δ 5.55 (m, 2H), 3.01 (m, 2H), 2.45-2.39 (m, 2H), 2.15-1.98 (m, 6H); ^{13}C NMR (100 MHz, CDCl₃) δ 129.04, 56.93, 28.30, 23.87. ^1H -NMR data is agreement with data given in the literature.¹¹

Acknowledgements

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