

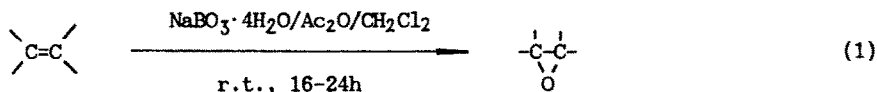
SODIUM PERBORATE OXIDATIONS OF CYCLIC AND ACYCLIC ALKENES
 TO OXIRANES OR VICINAL ACETOXY ALCOHOLS

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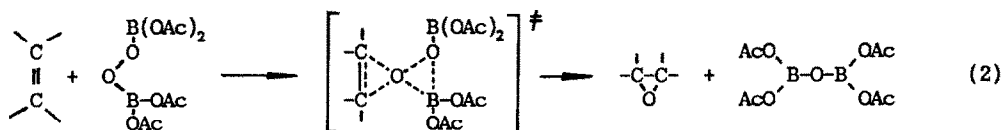
Abstract: Under different reaction conditions, sodium perborate/acetic anhydride oxidizes alkenes into oxiranes or vicinal acetoxy alcohols in good yields.

Sodium perborate ($\text{NaBO}_3 \cdot n\text{H}_2\text{O}$, $n=1-4$) is a very cheap and widely used industrial chemical. However, its utilization in organic synthesis has not received much attention. There have only been a few reported reactions using it as an oxidant, such as the cleavage of 1,2-diketones [1], the oxidation of alkenylboronic acids [2], the oxidations of anilines to azo compounds or nitroarenes and sulfides to sulfoxides or sulfones [3,4]. The epoxidation by use of sodium perborate was also reported, but it was limited only to quinones [5]. Herein, we would like to report the oxidations of alkenes using sodium perborate and acetic anhydride.

When acetic anhydride was added to a mixture of sodium perborate and alkenes in dichloromethane, slightly exothermic reactions took place at room temperature and gave the epoxides in good yields after ca. 16-24 hours (Eq. 1, Table 1). Addition of catalytic amounts of concentrated sulfuric acid to the reaction mixtures shortened the reaction time, but the yields of the oxiranes were somewhat lower.













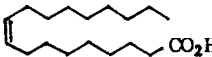



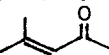
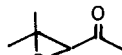
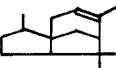
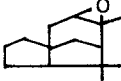


Like the reaction of sodium borate with acetic anhydride which gives the triacetoxyborane or oxybis(diacetoxy)borane [6], the reaction of sodium perborate with acetic anhydride may form a boron acetate intermediate containing a peroxy bond which then reacts with the alkenes to give the corresponding oxiranes. In fact, peroxybis(diacetoxy)borane, $(\text{AcO})_2\text{B}-\text{O}-\text{B}(\text{OAc})_2$ [7], which is easily soluble in most organic solvents and explosive when heated, was isolated from the reaction mixture. Although the mechanism for the present epoxidation is still unclear, a possible mechanism is shown in Eq. 2. The transition state of the reaction may be similar to that of the epoxidation of alkenes by organic peroxy acid.



When acetic anhydride was used as the solvent and concentrated sulfuric acid (5% of acetic anhydride by volume) was added dropwise into the reaction mixture of sodium perborate and alkenes, highly exothermic reactions occurred to result in the corresponding vicinal acetoxy alcohols (Eq. 3, Table 2).


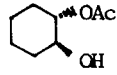
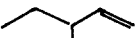
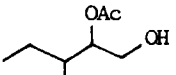

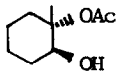

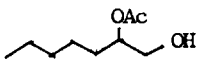

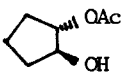
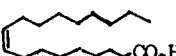
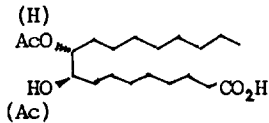


Table 1: Oxiranes from Epoxidation of Alkenes by Sodium Perborate in Dichloromethane^a

Alkene	Epoxide	Yield(%)	Alkene	Epoxide	Yield(%)
		75			46(25 ^b)
		65			50(15 ^b)
		68			60
		73			45
		72			70

a: All epoxides obtained gave IR and ¹H-NMR spectra which were identical with those of authentic samples. b: Yield of the mono-epoxide.

Table 2: Vicinal Acetoxy Alcohols from Oxidation of Alkenes by Sodium Perborate in Ac₂O^a

Alkene	Acetate	Yield(%)	Alkene	Acetate	Yield(%)
		72			50
		71			48
		59			64 ^b

a: All vicinal acetoxy alcohols were detected by IR, ¹H-NMR and MS. b: A mixture of 9-hydroxyl and 10-hydroxyl isomers.

Thus, sodium perborate may be used as an alternative reagent for the epoxidation of alkenes. In addition, the oxidation of alkenes by it in the presence of sulfuric acid also provides a convenient method for the preparation of the vicinal acetoxy alcohols from olefins directly.

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References and Notes

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- [7] A hygroscopic white crystalline product was obtained. m.p. 26°C; IR(nujol): 1740 (C=O)cm⁻¹; ¹H-NMR, δ: 1.9 (s, CH₃)ppm; C₈H₁₂B₂O₁₀, cacl: C, 33.16%, H, 4.18%, found: C, 33.64%, H, 4.33%.

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