

Efficient Epoxidation of α,β -Enones with Polyvinylpyrrolidone Supported Hydrogen Peroxide (PVP-H₂O₂)

Ali Reza Pourali* and Mersieh Ghanei

Department of Chemistry, Damghan University of Basic Sciences, Damghan 36715/364, Iran. *E-mail: pourali@dubs.ac.ir

Received July 18, 2006

Key Words : Epoxidation, Hydrogen peroxide, Polymer supported reagents, α,β -Unsaturated ketones

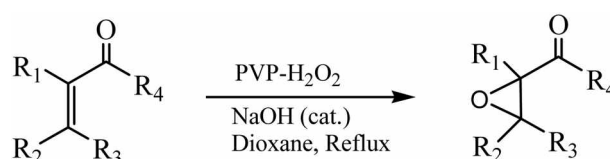
Organic peroxides are frequently used as oxidants in organic synthesis especially for the epoxidation of electron-deficient alkenes *e.g.* α,β -unsaturated carbonyl compounds.¹ Alkaline solutions of hydrogen peroxide and *tert*-butyl hydroperoxide are powerful nucleophilic oxidizing agents for this purpose.² In the epoxidation of α,β -enones, peroxides are superior reagents to organic peracids with respect to their mildness, good yields and absence of by-products. Epoxidation of electron-deficient alkenes is normally sluggish with electrophilic oxidizing agents such as mCPBA.

While hydrogen peroxide has been used frequently for oxidation of organic compounds, there is some hazard connected with the use of concentrated solutions of H₂O₂. On the other hand, general interest is the development of new clean oxidation methods which can supply the needs for improvements in epoxide synthesis. Generally, these needs concern more selective epoxidation methods with preferably heterogeneous recyclable, and with safe, clean and regenerable oxidants. Two complexes of H₂O₂ with urea (UHP) and DABCO-di-N-oxide are known reagents³ but they have some limitations involved in the selection of proper solvent to conduct the reactions under heterogeneous conditions.

Polymer supported reagents have had much attentions in recent years due to their selectivity, stability and easy handling.^{4,6} They could serve as heterogeneous, clean and regenerable reagents in the epoxidation reactions. Preparation of polymer complexes of hydrogen peroxide was also reported⁷ but we could not find any synthetic use in the literature. Also the epoxidation of olefins with a crosslinked polystyrene-supported *tert*-butyl hydroperoxide have been investigated but it suffers from low yields, low selectivity and long reaction times.⁸ A number of epoxidation methods have been developed for α,β -unsaturated carbonyl compounds which involve sodium peroxide,⁹ Keggin heteropoly compounds with aqueous H₂O₂ in acetonitrile,¹⁰ hydrogen peroxide in ionic liquid/water biphasic system,¹¹ urea-hydrogen peroxide,¹² dioxirane^{13,14} and many asymmetric methods.¹⁵ In this paper we report an efficient epoxidation of α,β -enones with a polymer supported hydrogen peroxide under heterogeneous conditions.

Results and Discussion

We recently reported the use of polyvinylpyrrolidone supported hydrogen peroxide (PVP-H₂O₂) as a stable and

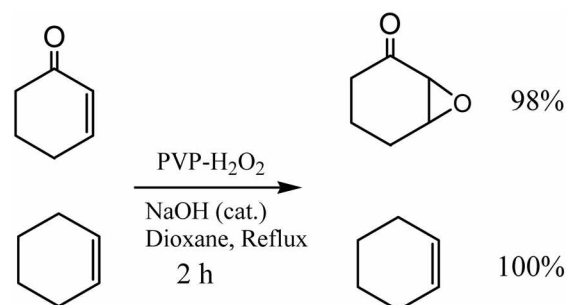


Scheme 1

recyclable solid oxidant in the presence of KI or I₂ for iodination of some activated aromatic compounds.¹⁶ This reagent could be dried as a solid and powdered in a mortar. The capacity of PVP-H₂O₂ was determined to be 7.5 mmol of H₂O₂ per gram of the solid reagent. The reagent could be stored in refrigerator for several months without loss of its weight or activity.

In this procedure, various α,β -unsaturated carbonyl compounds were reacted with PVP-H₂O₂ in the presence of few drops of NaOH in dioxane under reflux conditions (Scheme 1).

We first optimized the epoxidation reaction with 2-cyclohexene-1-one as a model, and then applied the conditions for other enones (Table 1). Under these conditions 2-cyclohexene-1-one was converted to 2,3-epoxy cyclohexanone in 98% isolated yield after 20 min. (Table 1, entry 8). Polyvinylpyrrolidone can be recycled and reused by a simple filtration after completion of the reaction. As shown in Table 1, most of the α,β -unsaturated carbonyl compounds were cleanly converted into the corresponding epoxides in good to excellent yields. Epoxides of simple olefins were obtained in poor yields (Table 1, entries 11, 12). This method showed excellent selectivity between 2-cyclohexene-1-one and cyclohexene. 2,3-Epoxy cyclohexanone was obtained with 98%



Scheme 2

Table 1. Conversion of carbon-carbon double bonds to epoxides with PVP-H₂O₂ in dioxane under reflux conditions

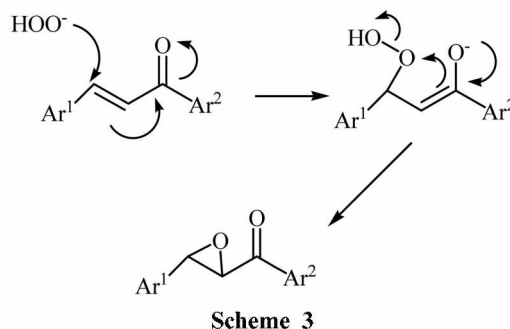
Entry	Substrate	Product ^a	reagent/ substrate molar ratio	Time (h)	Yield ^b (%)
1			3:1	3.5	96
2			4:1	5	90
3 ^c			4:1	4	65
4			3:1	5	80
5			4:1	6	87
6			3:1	1	91
7			3:1	3	85
8			3:1	20 min.	95
9 ^d			3:1	15 min.	98
10			3:1	2	96
11			4:1	24	25
12			4:1	24	30

^aAll products are known compounds and were identified by comparison of their physical or spectral data with those of authentic samples. ^bIsolated yield. ^cwithout addition of NaOH. ^droom temperature

yield in the presence of cyclohexene after 2 h in refluxing dioxane while cyclohexene was remained intact (Scheme 2).

In Scheme 3 a plausible mechanism for the reaction is proposed involving formation of HOO⁻ and a nucleophilic attack of HOO⁻ on α,β -unsaturated carbonyl compound.

We observed that without adding NaOH the reaction was slow and yields were low for example in the absence of



NaOH 2-cyclohexene-1-one was converted to 2,3-epoxy cyclohexanone in 35% isolated yield after 60 min. with PVP-H₂O₂ in dioxane under reflux conditions.

In conclusion, PVP-H₂O₂ is a stable and eco-friendly reagent for the selective, clean and safe epoxidation of α,β -unsaturated carbonyl compounds. High reaction yields, mild reaction conditions, simple setup and workup procedure are additional merits of our protocol.

Experimental Section

General. Polyvinylpyrrolidone K-30 (*M_w*, 40,000) was purchased from Fluka chemical company and other chemicals were obtained from Merck chemical company. The progress of the reaction was monitored by thin-layer chromatography on commercial Merck precoated TLC plates (silica gel 60 F₂₅₄) or by GLC on a Shimadzu model GC 10-A instrument. All products are known and they are identified by comparison of their physical and spectroscopic data with those of authentic samples after purification by column chromatography. Melting points were determined in open capillary tubes with a Buchi 510 apparatus. FT-IR spectra were recorded on a Perkin Elmer RXI spectrometer.

Preparation of polyvinylpyrrolidone supported hydrogen peroxide (PVP-H₂O₂). To a solution of 30% H₂O₂ (6 mL) at 0 °C was added polyvinylpyrrolidone K-30 (2 g) while the solution was gently stirred. After 1 h, the resulting solution was poured into a plate and dried overnight at room temperature. Then, the dried solids were powdered in a mortar. The capacity of the reagent was determined to be 7.5 mmol of H₂O₂ per gram of the solid reagent. The reagent could be stored in the refrigerator for several months without loss of its weight or activity.

Typical procedure; conversion of 2-cyclohexene-1-one to 2,3-epoxy cyclohexanone with PVP-H₂O₂. To a solution of 2-cyclohexene-1-one (0.096 g, 1 mmol) in dioxane (5 mL), were added PVP-H₂O₂ (0.4 g, 3 mmol) and 4 drops of aqueous solution of NaOH (0.1 Mol/L). The mixture was refluxed and the progress of the reaction was monitored by TLC. After 20 min. the reaction mixture was filtered. Extraction of mixture by dichloromethane (3 × 10 mL) and column chromatography on silica gel by using petroleum ether-ethyl acetate (2 : 1) as eluent gave 2,3-epoxy cyclohexanone (0.106 g, 95% yield).

Acknowledgement. Financial support by DUBS Research Council is gratefully acknowledged.

References

1. Rao, A. S. In *Comprehensive Organic Synthesis*; Trost, B. M.; Fleming, I., Eds.; Pergamon Press: Oxford, 1991; Vol. 7.
 2. Carruthers, W.; Coldham, I. *Modern Methods of Organic Synthesis*, 4th ed.; University press: Cambridge, 2005; Chapter 5.
 3. Heaney, H. In *Novel Organic Peroxygen Reagents for Use in Organic Synthesis*, Top. Curr. Chem. Series 164, Organic Peroxygen Chemistry; Herrmann, W. A., Ed.; Springer-Verlag: Berlin, 1993.
 4. Ley, S. V.; Baxendale, I. R.; Bream, R. N.; Jackson, P. S.; Leach, A. G.; Longbottom, D. A.; Nesi, M.; Scott, J. S.; Storer, R. I.; Taylor, S. J. *J. Chem. Soc., Perkin Trans. 1* **2000**, 3815.
 5. Iranpoor, N.; Firouzabadi, H.; Pourali, A. R. *Synthesis* **2003**, 1591.
 6. Iranpoor, N.; Firouzabadi, H.; Pourali, A. R. *Tetrahedron* **2002**, 58, 5179.
 7. Panarin, E. F.; Kalninskii, K. K.; Azanova, V. V. *Polymer Science (A)* **2000**, 42, 522.
 8. Sheela, M. S.; Sreekumar, K. *J. Chem. Sci.* **2004**, 116, 319.
 9. Reddy, V. K.; Haritha, B.; Yamashita, M. *Lett. Org. Chem.* **2005**, 2, 128.
 10. Qiang, G.; Yong, D.; Haitao, L.; Jishuan S. *J. Chem. Res.* **2005**, 716.
 11. Wang, B.; Kang, Y. R.; Yang, L. M.; Suo, J. S. *J. Mol. Cat. (A): Chemical* **2003**, 203, 29.
 12. Santos, A. A.; Wendler, E. P.; Marques, F. A.; Simonelli, F. *Lett. Org. Chem.* **2004**, 1, 47.
 13. Curci, R.; Dinoi, A.; Rubino, M. F. *Pure Appl. Chem.* **1995**, 67, 811.
 14. Wang, Z.-X.; Miller, S. M.; Anderson, O. P.; Shi, Y. *J. Org. Chem.* **1999**, 64, 6443.
 15. Porter, M. J.; Skidmore, J. *Chem. Commun.* **2000**, 1215 and references cited therein.
 16. Pourali, A. R.; Ghanei, M. *Chin. J. Chem.* **2006**, 24, 1077.
-