

Study on catalytic epoxidation of olefins in ketone-hydrogen peroxide system

Xiao-hui Xu^{1,a}, Yue-yue Wang^{1,b}, Fu-ping Zheng^{1,2,c*}, Teng Zhang^{1,d}, Yu-ping Liu^{1,2,e}, Bao-guo Sun^{1,2,f}

¹Beijing Laboratory for Food Quality and Safety, Beijing Technology and Business University, Beijing 100048, China

²Beijing Innovation Centre of Food Nutrition and Human Health, Beijing Technology and Business University, Beijing 100048, China

^axxh4852506@163.com, ^byyw632591@163.com, ^czhengfp@btbu.edu.cn,

^d348900359@qq.com, ^eliuyp@th.btbu.edu.cn, ^fsunbg@btbu.edu.cn

Keywords: Olefins; Epoxidation; Ketone - hydrogen peroxide system; Epoxides

Abstract. Epoxides are important intermediates in organic synthesis, ketone-hydrogen peroxide was a clean and efficient catalytic oxidant for the epoxidation of olefins. Eleven ketone- hydrogen peroxide systems were used in the epoxidation of α -pinene to 2,3-epoxypinane, acetone- hydrogen peroxide system gave the best yield and selectivity (91.8% and 97.5% in turn) among the eleven systems. Other two kinds of terpenes, three kinds of aromatic olefins, and three kinds of cycloolefins were oxidized under the acetone-hydrogen peroxide system with yields among 72.6% to 93.2%. For aromatic olefins and cycloolefins, the reactant with the electron-donating group gave a higher yield than those with the electron-withdrawing group.

Introduction

Epoxides of terpenes, aromatic olefins and cycloolefins are important intermediates in the synthesis of fragrance/flavor compounds and other fine chemicals. For example, the epoxide of α -pinene can be used to synthesize a series of fragrance/flavor compounds, such as 3-pinanol^[1], 3-pinone^[2], baccanol^[3], sandalore^[4] (as shown in Fig 1). The epoxide of β -pinene were intermediate to synthesize perilla alcohol and its derivatives^[5-7]. 2-Phenylethanol^[8] and phenylacetaldehyde^[9] were synthesized by the epoxidation of styrene; catechol was synthesized by the epoxidation of cyclohexene^[10].

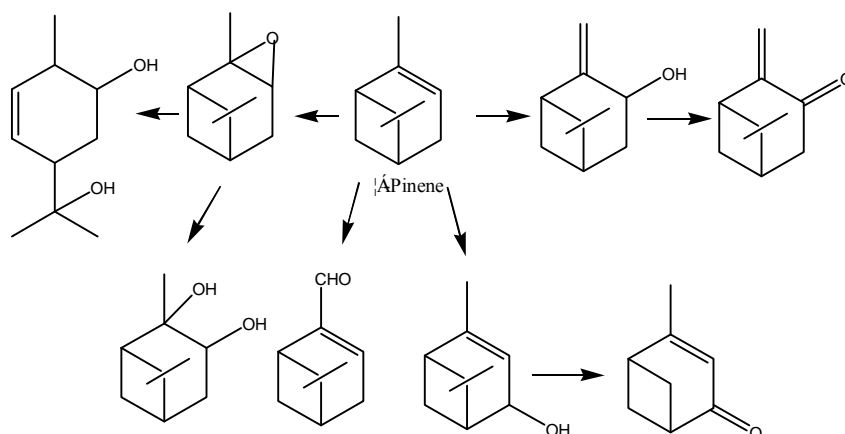


Fig 1. α -Pinene and its several derivatives

In the past few years, the common oxidant of epoxidation were Oxone ($2\text{KHSO}_5 \cdot \text{KHSO}_3 \cdot \text{K}_2\text{SO}_4$)^[11-14] and peracetic acid^[15]. The disadvantages of Oxone were large solid waste emission^[16]. Peracetic acid were unstable and easy to decompose; it should be used as soon as possible once it was prepared. Transition metal compounds were used as epoxidation agents in some cases, such as manganese sulfate(MnSO_4)^[17], methyltrioxorhenium (MeRO_3 or MTO)^[18], tungsten superoxide anion salt ($\{[\text{W}(=\text{O})(\text{O}_2)_2(\text{H}_2\text{O})]_2(\mu\text{-O})\}^{2-}$)^[19], coordination compound of molybdenum (positive ion was tetraphenylphosphonium $[\text{PPh}_4]^+$, negative ion was $[\text{MoO}(\text{O}_2)_2(\text{saloxH})]^-$)^[20]. The high price and usually high toxicity of most transition metals limit their applications in epoxidation reactions. Hydrogen peroxide was an environmentally friendly oxidant because it would turn into water after the reaction, without the emission of other wastes. Lian-he Shu and Yi-an Shi^[21] reported the epoxidation of olefins in catalytic systems of different ketones-hydrogen peroxide and found that the highest conversion of olefins can be obtained when the catalytic system was trifluoroacetone-hydrogen peroxide. However, the low boiling point of trifluoroacetone (21.9 °C) usually limit its application in the reactions under room temperature or reflux, even ignoring its high price. The screening of an inexpensive and effective catalytic system become important for the epoxidation reaction. Xiang-wen He, et al. of our team, reported the epoxidation of the α -pinene in acetone-hydrogen peroxide catalytic system and gave an optimized yield of 86.8% of 2,3-epoxypinane^[22]. Acetone is a cheap reagent and has a proper boiling point (56.1 °C), compared with trifluoroacetone. The mechanism of the catalytic system of ketone-hydrogen peroxide in epoxidation was shown in Fig 2.^[21]

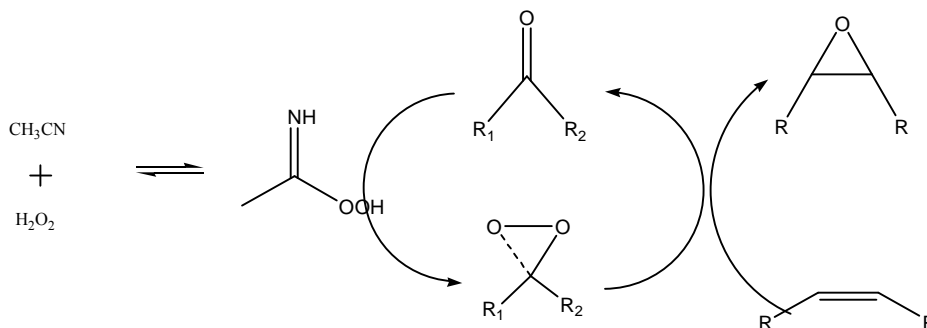


Fig 2. The mechanism of catalytic system of ketone-hydrogen peroxide in epoxidation

Experimental

In this paper, 11 catalytic systems of ketones-hydrogen peroxide were studied in the epoxidation of α -pinene (Fig 3.). The dosage of α -pinene was 3.40g(25mmol), $n(\text{H}_2\text{O}_2) : n(\alpha\text{-pinene}) = 5 : 1$. The pH was adjusted to 10 by adding the powder of sodium bicarbonate, the ratio of acetonitrile to deionized water =4:1(in volume), the total volume of the reaction system was 100 mL. The reaction was carried out at 40 °C for 4 h. The mixture was extracted three times with CH_2Cl_2 , dried with anhydrous Na_2SO_4 . The solvent was removed under reduced pressure.

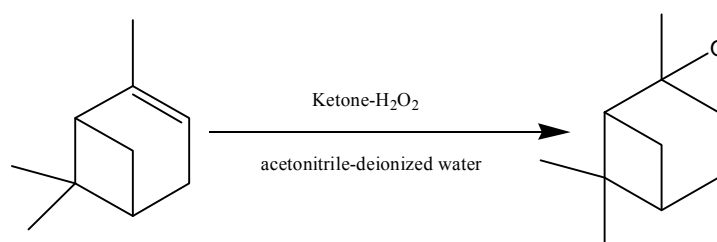


Fig 3. The epoxidation of α -pinene

Based on the optimized reaction condition of the epoxidation of α -pinene, two kinds of terpenes, three kinds of aromatic olefins and three kinds of cyclenes were epoxidized, which including: β -pinene(**a**), camphene(**b**), 4-methylstyrene(**c**), styrene(**d**), 4-chlorostyrene(**e**), 4-methylcyclohexen(**f**), cyclohexene(**g**) and 3-cyclohexen-1-carboxylic acid (**h**).

The structure of the epoxides was determined by data of MS from GC/MS; the molecular formulae were further determined by data of accurate mass from high-resolution TOF MS. The yields and selectivity of 2,3-epoxypinane were calculated from data of GC.

2,3-Epoxy-pinane, MS: m/Z (%):152(1, M), 137(41),119(11), 109(64), 83(45), 67(100), 55(40), 41(60), 27(17). Accurate Mass (molecular formula): 152.117830 (C₁₀H₁₆O).

a: MS: m/Z (%): 152(1, M), 137(36), 123(53), 109(53), 91(36), 79(100), 67(55), 55(48), 41(80). Accurate Mass (molecular formula): 152.119802 (C₁₀H₁₆O).

b: MS: m/Z (%):151(4, M-1), 131(100), 123(6),119(2), 109(38), 105(12), 94(50), 89(17), 67(20), 55(12), 41(25), 37(17), 27(9). Accurate Mass (molecular formula): 152.115408 (C₁₀H₁₆O).

c: MS: m/Z (%):134(31, M), 119(13), 105(100),91(31), 63(3), 51(6), 39(3), 27(2),17(16). Accurate Mass (molecular formula): 134.072164 (C₉H₁₀O).

d: MS: m/Z (%):119(57, M-1), 105(2),91(100), 77(9),51(14), 45(1), 39(17),29(3). Accurate Mass (molecular formula): 120.055969 (C₈H₈O).

e: MS: m/Z (%): 154(40, M), 139(3), 125(100), 119(67), 111(3), 99(6), 89(83), 75(6), 63(17), 39(6), 29(3). Accurate Mass (molecular formula): 154.016107 (C₈H₇OCl).

f: MS: m/Z (%): 111(5, M-1), 97(100), 84(52), 55(52), 43(29),41(90). Accurate Mass (molecular formula): 112.087733 (C₇H₁₂O).


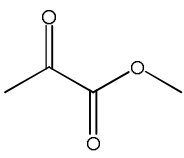
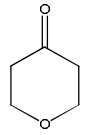
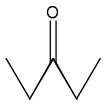
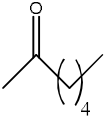
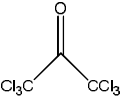
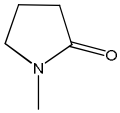
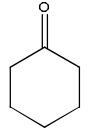
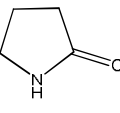
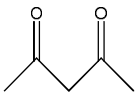
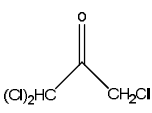
g: MS: m/Z (%): 97(14, M-1), 83(100), 79(7), 69(26), 65(3), 54(43), 41(71), 31(3), 27(29). Accurate Mass (molecular formula): 98.072835 (C₆H₁₀O).

h: MS: m/Z (%): 142(9, M), 124(100), 114(15), 100(30), 82(30), 70(72), 63(2), 55(39), 44(76), 38(42), 29(32). Accurate Mass (molecular formula): 142.061231 (C₇H₁₀O₃).

Results and discussion

The yields and selectivity of 2,3-epoxypinane in the epoxidation of α -pinene by ketones-hydrogen peroxide systems were shown in Table 1.

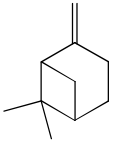
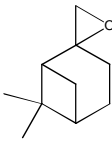
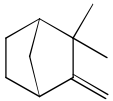
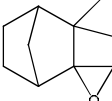
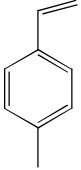
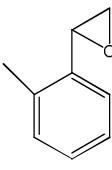
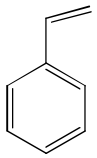
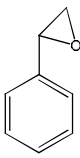
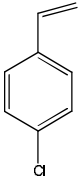
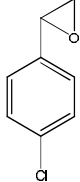
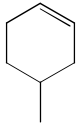
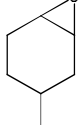
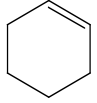
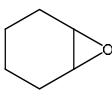
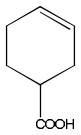
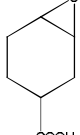
Table 1. Yields and selectivity of 2,3-epoxypinane by epoxidation of α -pinene in ketones -hydrogen peroxide systems

Entry	Ketone	Yield/%	Selectivity/%
1		91.8	97.5
2		90.2	94.9
3		78.1	96.0
4		72.7	81.5
5		64.8	81.8
6		62.8	67.5
7		60.3	69.1
8		60.2	82.2
9		56.0	61.6
10		53.2	59.9
11		23.7	30.5

According to Table 1, the optimized yield of 2,3-epoxypinane was 91.8% with the selectivity of 97.5% when the epoxidation was carried out in acetone-hydrogen peroxide catalytic system (Entry 1). Methyl pyruvate-hydrogen peroxide system ranked top 2 with a yield of 90.2% and selectivity of 94.9% of 2,3-epoxypinane (Entry 2). Tetrahydro-4*H*-pyran-4-one -hydrogen peroxide system gave a yield of 78.1% and a high selectivity of 96.0% (Entry 3) which are greater than those of cyclohexanone (yield of 60.2%, selectivity of 82.2%, Entry 8) evidently due to the existence of

electron withdrawing oxygen atom(s) on the tetrahydropyran ring. But some ketones with electron withdrawing multi-chlorine atoms(hexachloroacetone, 1,1,3-trichloroacetone) (Entry **6** and **11**) or carbonyl groups (2,4-pentanedione, Entry **10**) did not give high yields or selectivity partly because of the stereo-hindrance effect of multi-chlorine atoms or carbonyl group. Other aliphatic ketones-hydrogen peroxide catalytic systems (Entry **4** and **5**) gave moderate yields of 2,3-epoxypinane (72.7% and 64.8% in turn) and selectivity of over 81%. The epoxidation of eight olefins was carried out in acetone-hydrogen peroxide system under the optimized reaction condition of that of α -pinane. The yields of the eight epoxides were shown in Table 2.

Table 2. The epoxidations products of eight olefins in acetone-hydrogen peroxide system

Entry	Olefin	Structure of Compound	Yield/%
a			93.2
b			91.6
c			88.5
d			87.3
e			82.5
f			89.4
g			78.7
h			72.6

As shown in Table 2, the epoxidation of terpenes under acetone-hydrogen peroxide system gave

satisfied yields of 91.6% and 93.2% (Entry **a** and **b**), that of aromatic olefins gave yields among 82.5% to 88.5% (Entry **c**, **d**, and **e**), and that of cycloolefins gave yields among 72.6% to 89.4% (Entry **f**, **g**, and **h**). Furthermore, the property of the substituent group has a great influence on the yield of the epoxides. For example, the electron-donating methyl group adding to cyclohexene could raise the yield of the epoxides from 78.7% to 89.4%; on the other hand, the electron-withdrawing carboxyl group adding to cyclohexene could decrease the yield from 78.7% to 72.6%. Similar effects exist on the epoxidation of aromatic olefins.

Conclusions

The catalytic epoxidation of α -pinene in ketone-hydrogen peroxide system was optimized by using 11 ketones. Acetone-hydrogen peroxide system shows satisfied effect with a yield of 91.8% and a selectivity of 97.5% of 2,3-epoxypinane. Other two kinds of terpenes, three kinds of aromatic olefins, and three kinds of cycloolefins were oxidized under the above optimized condition with yields of 72.6%-93.2%. For aromatic olefins and cycloolefins, the reactant with the electron-donating group gave a higher yield than that with the electron-withdrawing group.

Acknowledgement

This work was financially supported by the National Key Technology R & D Program, P. R. China (2011BAD23B01)

References

- [1] Fernández-Mateos, A., Teijón, P. H., González, R. R.. Radical reactions on pinene-oxide derivatives induced by Ti(III)[J]. *Tetrahedron*, 2011, 67(49): 9529-9534.
- [2] Salminen, E., Virtanen, P., et al. Isomerisation of α -Pinene Oxide to Campholenic Aldehyde Over Supported Ionic Liquid Catalysts [J]. *Topics in Catalysis*, 2014, 57(17-20):1533-1538.
- [3] Ma, H. L., Wu, Q. L., et al. The Development of Synthetic Sandalwood Compounds[J]. *Flavour Fragrance Cosmetics*, 2014, 1: 44-48.
- [4] Li, Ch. L., Mao, H. F., Pan, X. H.. The Development of Study on the Synthetic Sandalwood Compounds[J]. *Flavour Fragrance Cosmetics*, 2006, 2(1): 31-35. (In Chinese)
- [5] Justicia, J., Jiménez, T., Morcillo, S. P., et al. Mixed disproportionation versus radical trapping in titanocene(III)-promoted epoxide openings[J]. *Tetrahedron*, 2009, 65(52): 10837-10841.
- [6] Xia, K. J., Xia, L. Q.. Synthesis of Perillyl Aldehyde[J]. *Journal of Jiangxi Institute of Education*, 2006,27(6): 33-36. (In Chinese)
- [7] Li, Q. H., Yin, D. L., Xiao, Y., et al. Synthesis of Perillarine[J]. *Chinese Journal of Applied Chemistry*, 2000, 17(5): 536-538. (In Chinese)
- [8] Miyamoto, K., Tada, N., Ochiai, M.. Activated Iodosylbenzene Monomers as an Ozone Equivalent: Oxidative Cleavage of Carbon-Carbon Double Bonds in the Presence of Water[J]. *Cheminform*, 2007, 38(28).
- [9] Telvekar, V., Patel, D., Mishra, S.. Oxidative Cleavage of Epoxides Using Aqueous Sodium

- Paraperiodate[J]. Synthetic Communications, 2009, 39(2): 311-315.
- [10] Matsuoka, Kazuyuki. Manufacture of catechol and its derivatives[P]. Jpn, Kokai Tokkyo Koho. 1991. JP 03227946 A, Oct 08, 1991.
- [11] Wang, Z. X., Tu, Y., Frohn, M., et al. An Efficient Catalytic Asymmetric Epoxidation Method[J]. Journal of the American Chemical Society, 1997, 119(46): 11224-11235.
- [12] Dan, Y., Wong, M. K., Yip, Y. C., et al. Design And Synthesis Of Chiral Ketones For Catalytic Asymmetric Epoxidation Of Unfunctionalized Olefins[J]. Journal of the American Chemical Society, 1998, 120(24): 5943-5952.
- [13] Frohn, M., Zhixian Wang, A., Shi, Y.. A Mild and Efficient Epoxidation of Olefins Using in Situ Generated Dimethyldioxirane at High pH[J]. Journal of Organic Chemistry, 1998, 63(18): 6425-6426.
- [14] Yang, D., Yip, Y. C., Tang, M. W., et al. Novel Cyclic Ketones for Catalytic Oxidation Reactions[J]. Journal of Organic Chemistry, 1998, 63(26):9888-9894.
- [15] Zhang, Y. D., Jiang, D. G., Gao, X. L., et al. Study of Process for Synthesis of Epoxycyclohexane with t-Butyl Hydroperoxide as Oxidant[J]. Fine Chemicals, 2002, 19(5): 291-294. (In Chinese)
- [16] He, X. W, Zheng, F. P., Sun, B. G., et al. Epoxidation of beta-Pinene to 2,10- Epoxypinane by Oxone. [J]. Fine Chemicals, 2011, 4: 3152-3155.
- [17] Ho, C., Chen, Y., Wong, M., et al. Fluorinated chiral secondary amines as catalysts for epoxidation of olefins with oxone[J]. Journal of Organic Chemistry, 2005, 70(25): 898-906.
- [18] Saladino, R., Crestini, C., Andreoni, A., et al. A novel and efficient catalytic epoxidation of olefins and monoterpenes with microencapsulated Lewis base adducts of methyltrioxorhenium[J]. Tetrahedron, 2005, 61(5): 1069-1075.
- [19] Yamaguchi, K., Uchida, S., Yoshida, C., et al. Peroxotungstate immobilized on ionic liquid-modified silica as a heterogeneous epoxidation catalyst with hydrogen peroxide[J]. Journal of the American Chemical Society, 2005, 127(2): 530-531.
- [20] Gharah, N., Chakraborty, S., Mukherjee, A. K., et al. Highly Efficient Epoxidation Method of Olefins with Hydrogen Peroxide as Terminal Oxidant, Bicarbonate as a Cocatalyst and Oxodiperoxo Molybdenum(VI) Complex as Catalyst [J]. Chemical Communications, 2005, 36(16): 2630-2632.
- [21] Shu, L., Shi, Y.. An Efficient Ketone-Catalyzed Epoxidation Using Hydrogen Peroxide as Oxidant[J]. Journal of Organic Chemistry, 2000, 32(17): 8807-8810.
- [22] He, X. W., Zheng, F. P., Xu, C. C., et al. Synthesis of 2,10-Epoxypinane by Epoxidation of β -Pinene with Hydrogen Peroxide[J]. Fine Chemicals, 2011, 28(10): 978-981. (In Chinese)