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A Practical Method for Epoxidation of Terminal Olefins with 30% Hydrogen Peroxide under Halide-Free Conditions

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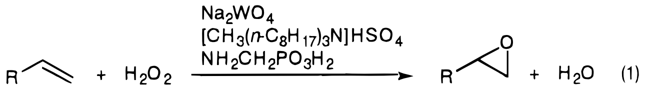
Epoxidation of olefins is among the most important reactions in organic synthesis,[1] because epoxy compounds are widely used as intermediates in the laboratory and for chemical manufacturing.[2] There is an ever increasing demand for a practical efficient procedure. Epoxidation of terminal olefins is the most important but difficult. Industry in particular, requires high yield, high selectivity, sufficient productivity, low cost, safety, operational simplicity, and environmental consciousness among other technical factors. In this context, Venturello's procedure using aqueous H_2O_2 as the oxidant[3] is appreciated, because water is the sole expected side product.[4] However, the original procedure for 1-octene epoxidation using a Na_2WO_4−H_3PO_4−quaternary ammonium chloride combined catalyst was unsatisfactory, since the reaction necessitated an excess of olefinic substrates in a 1,2-dichloroethane−water biphasic system giving the epoxy product in at most 53% yield. Since then a number of modified procedures have appeared,[5] and Ishii among others made a great improvement by using a tungsten-based heteropoly acid and *N*-cetylpyridinium chloride in a chloroform−water mixture raising the yield up to 80%.[6] Even the best procedure, however, requires toxic and carcinogenic chlorinated hydrocarbon solvents[7] to obtain a high yield and high selectivity (yield was only 33% in refluxing benzene[6]), defeating the environmental and economic advantages of H_2O_2 as the oxidant.[4,8,9] We now disclose a very practical method that overcomes this serious problem (eq 1).

Table 1. Epoxidation of Terminal Olefins with 30% Hydrogen Peroxide[a]

entry	olefin	mmol	Na_2WO_4, mmol	toluene, mL	time, h	convn,[b] %	yield,[b,c] %
1	1-octene	20	0.4	4	4	96	94
2		20	0.4	0	2	89	86
3		100	2	30	4		86[d]
4	1-decene	20	0.4	4	4	99	99
5		20	0.4	0	2	94	93
6		100	2	30	4		91[d]
7	1-dodecene	20	0.4	4	4	98	97
8		20	0.4	0	2	87	87
9		100	2	30	4		92[d]
10		594	12	0	2		87[d]

[a] Reaction was run using 30% H_2O_2, olefin, $Na_2WO_4{\cdot}2H_2O$, $NH_2CH_2PO_3H_2$, and $[CH_3(n\text{-}C_8H_{17})_3N]HSO_4$ in a 150:100:2:1:1 molar ratio at 90 °C with stirring at 1000 rpm. [b] Determined by GC analysis. [c] Based on olefin charged. [d] Isolated by distillation.



(1)

Our new catalytic system consists simply of Na_2WO_4 dihydrate, (aminomethyl)phosphonic acid, and methyltri-*n*-octylammonium hydrogensulfate in a 2:1:1 molar ratio and is free from any organic or inorganic chlorides.[10] The biphasic epoxidation of simple terminal olefins can be carried out at 90 °C with 150 mol % of H_2O_2 and 0.2−2 mol % of the catalyst *without organic solvents* or alternatively by adding toluene. Terminal olefins, which are normally least reactive, were epoxidized in 94−99% yield with 2 mol % of the catalyst. Some examples are given in Table 1. The turnover numbers of the epoxidation were 150−200 per W atom. The reaction of 1-dodecene when conducted on a 100 g scale without toluene, gave, after simple distillation of the organic phase, 1,2-epoxydodecane in 87% yield.

The use of ammonium hydrogensulfate, rather than conventional chlorides,[3,5a,c−f,6,7,11] as phase transfer catalysts was crucial for the high reactivity; addition of NaCl significantly retarded the reaction. Other trialkylmethylammonium hydrogensulfates possessing C_6 to C_{10} alkyl chains were equally usable. The exact role of the α-amino phosphonic acid in facilitating the epoxidation remains unclear, since it is largely decomposed under the reaction conditions (^{31}P NMR). The reaction with β- or γ-amino phosphonic acids was much slower.

One drawback of this method is the difficulty encountered in the epoxidation of styrene (eq 1, $R = C_6H_5$) and its simple derivatives. Styrene was converted to the epoxide but the latter was very sensitive to hydrolytic decomposition that probably occurs at the aqueous/organic interface. Yield of the epoxide remained less than 23%.

Experimental Section

General and Materials. ^{1}H NMR spectra were recorded on a JEOL JNM-A400 NMR spectrometer at 400 MHz with tetramethylsilane used as an internal standard. The chemical shifts are reported in ppm on δ scale downfield from tetram-

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[9] For expoxidation in *tert*-butyl alcohol using H_2O_2 dried over Mg_2SO_4 see: (a) Herrmann, W. A.; Fischer, R. W.; Marz, D. W. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1638−1641. (b) Herrmann, W. A.; Fischer, R. W.; Rauch, M. U.; Scherer, W. *J. Mol. Catal.* **1994**, *86*, 243−266. In methanol: (c) Clerici, M. G.; Ingallina, P. *J. Catal.* **1993**, *140*, 71−83.

[10] For example, epoxy resin encapsulants for semiconductors are required to be entirely free from chlorides.

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S0022-3263(96)01287-X CCC: $12.00

ethylsilane, and signal patterns are indicated as follows: s, singlet; d, doublet; t, triplet; m, multiplet; br, broad peak. ^{13}C NMR spectra were measured on a JEOL JNM-A400 NMR spectrometer at 100 MHz. The chemical shifts are reported in ppm with chloroform-*d* (77.0 ppm) as an internal standard. Gas chromatographic analyses were performed on a Shimadzu GC-14A gas chromatograph.

Sodium tungstate dihydrate, aqueous 30% hydrogen peroxide, tri-*n*-octylamine, dimethyl sulfate, and toluene were obtained from Nacalai Tesque, Inc., and used as received. 1-Octene and 1-dodecene were purchased from Tokyo Kasei Kogyo Co., Ltd., and were distilled before use. 1-Decene was purchased from Aldrich Chemical Co. and purified by distillation before use. (Aminomethyl)phosphonic acid[12] was synthesized according to the literatures.

Preparation of Methyltri-*n*-octylammonium Hydrogensulfate. A 100-mL, round-bottomed flask equipped with a magnetic stirring bar was charged with 17.7 g (50.0 mmol) of tri-*n*-octylamine and 20 mL of toluene. Under stirring, 6.50 g (51.5 mmol) of dimethyl sulfate was added in portions at room temperature, and then the mixture was heated at 140 °C for 17 h. The dark red solution was mixed with 1.0 mL of water and heated at 90 °C for 12 h. The mixture was cooled to room temperature, 20 mL of 49% sulfuric acid was added, and the biphasic mixture was vigorously stirred for 12 h. Removal of volatile material in vacuo gave 23.4 g (99%) of methyltri-*n*-octylammonium hydrogensulfate.[13] ^1H NMR (400 MHz, $CDCl_3$) δ 0.88 (t, 9H, $J = 7.0$ Hz), 1.27−1.35 (m, 30H), 1.66 (br, 6H), 3.19 (s, 3H), 3.25 (t, 6H, $J = 8.0$ Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.0, 22.2, 22.5, 26.1, 28.9, 29.0, 31.6, 61.4.

Procedure for Hectogram-Scale Epoxidation of 1-Dodecene. A 1-L, round-bottomed flask equipped with a reflux condenser and a magnetic stirring bar was charged with 3.919 g (11.9 mmol) of $Na_2WO_4 \cdot 2H_2O$, 101.0 g (891 mmol) of aqueous 30% H_2O_2, 0.660 g (5.94 mmol) of $NH_2CH_2PO_3H_2$, and 2.767 g (5.94 mmol) of $[CH_3(n\text{-}C_8H_{17})_3N]HSO_4$, and the biphasic mixture was vigorously stirred at room temperature for 15 min. To this was added 100.0 g (594 mmol) of 1-dodecene, and the mixture was heated at 90 °C for 2 h with stirring at 1000 rpm and cooled to room temperature. The organic phase was separated, washed with 150 mL of saturated aqueous $Na_2S_2O_3$, and distilled through a short column under vacuum to give 96.20 g (87.2%) of 1,2-epoxydodecane as a colorless liquid, bp 73.5−77.0 °C/0.3 mmHg.[14,15] GC (column, OV-1, 0.25 mm x 50 m, GL Sciences Inc.); carrier gas, helium (1.2 kg/cm^2); initial column temp, 70 °C; final column temp, 280 °C; progress rate, 9 °C/min; injection temp, 280 °C; split ratio, 100:1; retention time (t_R) of 1-dodecene, 12.4 min; t_R of 1,2-epoxydodecane, 16.5 min. ^1H NMR (400 MHz, $CDCl_3$) δ 0.88 (t, 3H, $J = 6.7$ Hz), 1.27−1.54 (m, 18H), 2.46 (dd, 1H, $J = 2.9$, 4.9 Hz), 2.74 (dd, 1H, $J = 3.9$, 4.9 Hz), 2.89 (br, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.1, 22.7, 26.0, 29.4, 29.5, 29.6, 29.7, 32.0, 32.6, 47.1, 52.4.

1,2-Epoxyoctane.[16] GC (column, OV-1, 0.25 mm x 50 m, GL Sciences Inc.); carrier gas, helium (1.2 kg/cm^2); initial column temp, 70 °C; final column temp, 280 °C; progress rate, 5 °C/min; injection temp, 280 °C; split ratio, 100:1; t_R of 1-octene, 6.4 min; t_R of 1,2-epoxyoctane, 10.7 min. ^1H NMR (400 MHz, $CDCl_3$) δ 0.89 (t, 3H, $J = 6.8$ Hz), 1.29−1.55 (m, 10H), 2.46 (dd, 1H, $J = 2.9$, 4.9 Hz), 2.74 (dd, 1H, $J = 3.9$, 4.9 Hz), 2.89 (br, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.1, 22.6, 26.0, 29.1, 31.8, 32.5, 47.1, 52.4.

1,2-Epoxydecane.[17] GC (column, OV-1, 0.25 mm x 50 m, GL Sciences Inc.); carrier gas, helium (1.2 kg/cm^2); initial column temp, 70 °C; final column temp, 280 °C; progress rate, 9 °C/min; injection temp, 280 °C; split ratio, 100:1; t_R of 1-decene, 8.8 min; t_R of 1,2-epoxydecane, 14.4 min. ^1H NMR (400 MHz, $CDCl_3$) δ 0.88 (t, 3H, $J = 6.8$ Hz), 1.27−1.55 (m, 14H), 2.46 (dd, 1H, $J = 3.0$, 5.0 Hz), 2.74 (dd, 1H, $J = 3.9$, 5.0 Hz), 2.90 (br, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.0, 22.6, 25.9, 29.2, 29.4, 29.5, 31.8, 32.4, 47.0, 52.3.

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