A Halide-Free Method for Olefin Epoxidation with 30% Hydrogen Peroxide

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A catalytic system consisting of sodium tungstate dihydrate, (aminomethyl)phosphonic acid, and methyltrioctylammonium hydrogensulfate, effects the epoxidation of olefins using 30% hydrogen peroxide with a substrate-to-catalyst molar ratio of 50—500. The reaction proceeds in high yield *without solvents*, or, alternatively, with added toluene under entirely halide-free conditions. Lipophilic ammonium hydrogensulfate, which replaces the conventional chloride, and an (α-aminoalkyl)phosphonic acid are crucial for the high reactivity. This method is operationally simple, environmentally benign, and much more economical than the oxidation with *m*-chloroperbenzoic acid, allowing for a large-scale preparation of epoxides. Various substrates including terminal olefins, 1,1- and 1,2-disubstituted olefins, cyclic olefins, and tri- and tetrasubstituted olefins as well as allylic alcohols, esters, α,β-unsaturated ketones, and ethers can be epoxidized in high yield. The scope and limitations of this new reaction system are discussed.

Epoxides are a versatile class of compounds for the laboratory and industrial manufacturing of a wide variety of chemicals, such as epoxy resins, surfactants, paints, adherents, reaction diluents, and surface-coating agents, in addition to a range of bioactive substances.[1)] Terminal epoxides are particularly important for preparing commodity chemicals, while the more substituted epoxides are useful for the synthesis of structurally more elaborated fine chemicals. Although olefin epoxidation is thought to be a matured chemistry, a truly effective method still remains elusive. Although alkali base-promoted dehydrochlorination of chlorohydrins is a major method for producing epoxides, it cannot be ideal. This procedure forms an equimolar amount of alkali metal chloride; also, the epoxy products are inevitably contaminated with organic or inorganic chlorides. The latter issue is sometimes problematic; epoxy-resin encapsulants for semiconductors, for example, are required to be absolutely free from chlorides.[1b)] Direct epoxidation of olefins is obviously more desirable than the two-step procedure. While various oxidants are now being used for both laboratory and industrial epoxidation,[2)] they are often hazardous and expensive, preventing their use for any large-scale reactions. In addition, most oxidants form equimolar amounts of the deoxygenated compounds as waste, which are difficult to remove from the epoxide products. The goal of modern organic synthesis is to develop efficient catalytic methods that can produce desired compounds in a cost-effective and environmentally benign manner. The olefin epoxidation procedure must be high-yielding and with high selectivity without any by-products through a simple, safe operation using a clean, well-behaving, and cheap oxidant. In this context aqueous 30% hydrogen peroxide, viewed as an adduct of oxygen atom and water, is an ideal oxidant. The atom efficiency is excellent and water is a sole theoretical side product.[3)] An additional practical benefit of this oxidant is the low transport cost due to the small volume and high density.

Currently, tungsten-based compounds are the most effective as catalysts for epoxidation using aqueous hydrogen peroxide. In 1959, Payne and Williams reported on the epoxidation of 2-heptene, a 1,2-disubstituted olefin using sodium tungstate as a catalyst.[4)] Venturello and co-workers found that less reactive terminal olefins are epoxidized effectively with 8% hydrogen peroxide in the presence of catalytic amounts of sodium tungstate, phosphoric acid, and quaternary ammonium chloride in a 1,2-dichloroethane–water mixture.[5)] Although the epoxidation is considered to proceed via peroxo tungsten complexes,[6—9)] the mechanistic details are unknown. The Venturello's procedure required an excess of the olefinic substrate; the yield of the epoxide based on the olefin did not exceed 53%. Since then, intense technical efforts have been made to improve the performance of this significant synthetic reaction. Most importantly, Ishii and co-workers found that a tungsten-based heteropoly acid combined with *N*-hexadecylpyridinium chloride catalyzes epoxidation with aqueous 35% hydrogen peroxide under organic–aqueous biphasic conditions using chloroform as the organic solvent, raising the yield up to 80%.[10)] Despite extensive studies on the biphasic epoxidation reaction,[5—15)] however, the use of chlorocarbon solvents was necessary for obtaining a high yield and high selectivity regardless the catalysts and reaction conditions. The possible injurious influences of chlorocarbons on health and the environment[16)] defeat the environmental and economic benefits of aqueous hydrogen peroxide being used as the oxidant. Although this

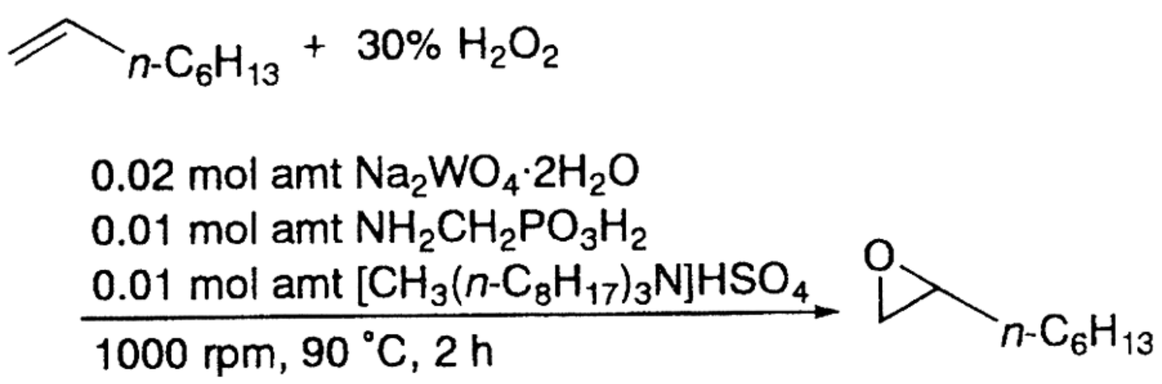
Dedicated to Professor Dieter Seebach, Eidgenössische Technische Hochschule, Zürich, on the occasion of his 60th birthday.

solvent problem has encouraged chemists to develop a new oxidation procedure without such solvents,[7] the highest yield in 1-octene epoxidation in refluxing benzene remained only 33%.[10]

Described herein is the current stage of our effort made along this line. The new epoxidation method is highly productive and practical. The reaction overcomes the major serious problem, and can be accomplished under entirely halide-free conditions, even without an organic solvent.[17] In addition, the epoxidation exhibits various unique selectivities that are unobserved in conventional epoxidations.

Results and Discussion

Epoxidation Conditions. We first searched for conditions to epoxidize the terminal olefins *without a solvent and any halides*. We tested various additives that might enhance the rate of epoxidation of 1-octene using 30% hydrogen peroxide (olefin : H_2O_2 molar ratio = 1 : 1.5), a 0.02 molar amount of sodium tungstate, and a 0.01 molar amount of methyltrioctylammonium hydrogensulfate at 90 °C with stirring at 1000 rpm (Eq. 1).[17] In the absence of any additive, 1,2-epoxyoctane was



(1)

obtained in only 5% yield after 2 h. As listed in Table 1, phosphoric acid and phenylphosphonic acid significantly accelerated the reaction, giving the epoxide in 63 and 52% yields, respectively, while (aminomethyl)phosphonic acid achieved the highest rate enhancement to reach 86% yield. Although (aminomethyl)phosphonic acid is largely (ca. 60%) decomposed under the reaction conditions to form mainly phosphoric acid, it facilitates the epoxidation more than does pure phosphoric acid for some unknown reason. The reaction with (2-aminoethyl)- and (3-aminopropyl)phosphonic acids, which are stable under the oxidation conditions, was much slower, however. The epoxidation proceeded equally well by added toluene as a solvent to give 1,2-epoxyoctane in 94% yield.

The lipophilicity of the phase-transfer agent is important. As shown in Table 2, tetrakis(decyl)ammonium hydrogensulfate and methyltrioctylammonium hydrogensulfate gave satisfactory results, while tetrabutylammonium hydrogensulfate was inactive. It was also revealed that the nature of the counter anions of the quaternary ammonium ions is important to obtain high reactivity, as illustrated in Table 2. Quaternary ammonium chlorides, such as methyltrioctylammonium chloride or *N*-hexadecylpyridinium chloride, which are widely used as a standard phase-transfer catalyst or surfactant,[18] were much less effective than the hydrogensulfates (22 and 11% vs. 86%). In fact, the addition of a fivefold amount of sodium chloride to the ammonium hydrogensulfate strongly retarded olefin epoxidation (Table 1, Entry 7). The addition of sodium sulfate did not significantly affect the reaction rate (Table 1, Entry 8) in spite of the relatively weak accelerating ability of methyltrioctylammonium sulfate (Table 2, Entry 7). Figure 1 compares the effects of the counter anions, hydrogensulfate vs. chloride, on the product yield as a function of the reaction time. The low efficiency of

Table 1. Effects of Additives on Epoxidation of 1-Octene[a]

Entry	Additive	Yield[b]/% Without solvent[c]	Yield[b]/% In toluene[d]
1	—	5	3
2	H_3PO_4	63	70
3	$C_6H_5PO_3H_2$	52	57
4	$NH_2CH_2PO_3H_2$	86	94
5	$NH_2CH_2CH_2PO_3H_2$	11	3
6	$NH_2CH_2CH_2CH_2PO_3H_2$	3	4
7	$NH_2CH_2PO_3H_2$ + NaCl (1 : 5)[e]	17	4
8	$NH_2CH_2PO_3H_2$ + Na_2SO_4 (1 : 5)[f]	69	72

a) Reaction was run using 30% H_2O_2, 1-octene, $Na_2WO_4 \cdot 2H_2O$, additive, 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. Based on 1-octene charged. c) Reaction was run for 2 h. d) Reaction in 4 mL of toluene for 4 h. e) Reaction with 0.05 molar amount of NaCl to 1-octene. f) Reaction with 0.05 molar amount of Na_2SO_4 to 1-octene.

Table 2. Effects of Phase-Transfer Catalysts on Epoxidation of 1-Octene[a]

Entry	Phase-transfer catalyst	Yield[b]/% Without solvent[c]	Yield[b]/% In toluene[d]
1	—	0	0.1
2	$[(n\text{-}C_{10}H_{21})_4N]HSO_4$	69	83
3	$[CH_3(n\text{-}C_8H_{17})_3N]HSO_4$	86	94
4	$[R_3(CH_3)N]HSO_4$[e]	71	91
5	$[(n\text{-}C_6H_{13})_4N]HSO_4$	4	36
6	$[(n\text{-}C_4H_9)_4N]HSO_4$	0	0.5
7	$[CH_3(n\text{-}C_8H_{17})_3N]_2SO_4$[f]	29	24
8	$[CH_3(n\text{-}C_8H_{17})_3N]Cl$	22	18
9	$[CH_3(n\text{-}C_8H_{17})_3N]Cl$[g]	7	3
10	$(n\text{-}C_{16}H_{33}NC_5H_5)Cl$[h]	11	7
11	$[(n\text{-}C_4H_9)_4N]Cl$	0	0.1
12	$[(n\text{-}C_{10}H_{21})_4N]OH$	2	4
13	$[(n\text{-}C_8H_{17})_4N]OH$	2	4
14	$[(n\text{-}C_4H_9)_4N]OH$	0	0
15	$[C_6H_5CH_2(C_2H_5)_3N]OH$	0	0

a) Reaction was run using 30% H_2O_2, 1-octene, $Na_2WO_4 \cdot 2H_2O$, $NH_2CH_2PO_3H_2$, and phase-transfer catalyst in a 150 : 100 : 2 : 1 : 1 molar ratio at 90 °C with stirring at 1000 rpm. b) Determined by GC analysis. Based on 1-octene charged. c) Reaction was run for 2 h. d) Reaction in 4 mL of toluene for 4 h. e) R is a mixture of C_6 to C_{10} alkyl chains. f) Molar ratio of 30% H_2O_2, 1-octene, $Na_2WO_4 \cdot 2H_2O$, $NH_2CH_2PO_3H_2$, and phase-transfer catalyst was 150 : 100 : 2 : 1 : 0.5. g) H_3PO_4 was used instead of $NH_2CH_2PO_3H_2$. h) *N*-Hexadecylpyridinium chloride.

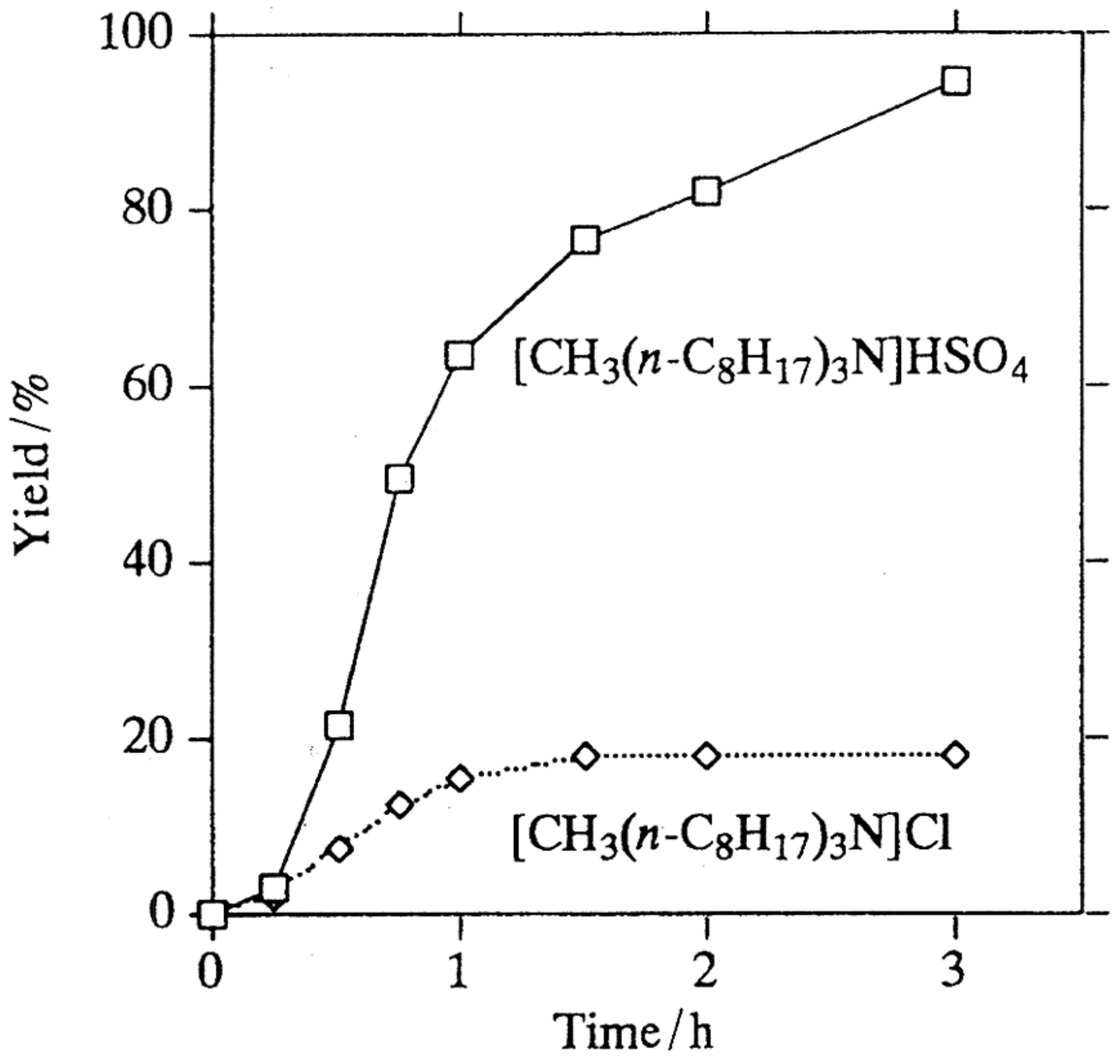


Fig. 1. Effect of the phase-transfer catalyst on the yield of epoxidation of 1-octene. Reaction was run using 30% H_2O_2, 1-octene, $Na_2WO_4 \cdot 2H_2O$, $NH_2CH_2PO_3H_2$, and phase-transfer catalyst in a 150 : 100 : 2 : 1 : 1 molar ratio at 90 °C with stirring at 1000 rpm.

the tetraalkylammonium chloride as a phase-transfer catalyst is probably due to an increase in the pH value of the aqueous phase as the reaction proceeds, as visualized in Fig. 2. When the hydrogensulfate is employed, the pH is maintained below 3 throughout the reaction.

Thus, terminal olefins were conveniently epoxidized in 94—99% yield using 30% hydrogen peroxide with a 0.02 molar amount of the tungsten catalyst under biphasic conditions.[17] The epoxidation of 1-dodecene on a 100 g scale without a solvent gave 1,2-epoxydodecane in 87% yield after simple distillation of the organic phase.

Catalytic Performance. Terminal olefins, such as 1-octene and 1-dodecene, are the least reactive substrates, while the internal olefins and cyclic olefins are epoxidized much more rapidly. As illustrated in Table 3, the catalytic performance of the present method compares well with those of the existing best procedures achieved in chlorocarbon solvents. Our catalyst system displays a turnover number as high as 150—450 per W atom in the epoxidation of terminal olefins without any organic solvent, and even 1600 with cyclooctene, a more reactive olefin (Entry 8). The reaction can be performed equally well by adding toluene, when this is more appropriate. Normally, the reaction without an or-

Table 3. Comparison of Activity of Catalyst Systems in Epoxidation with Aqueous Hydrogen Peroxide[a)]

Entry	Catalyst	Solvent	Turnover number[b)] (Temp/°C) 1-Octene		Cyclooctene		Ref.
1	$Na_2WO_4 \cdot 2H_2O$,[c)] H_3PO_4, $[CH_3(n\text{-}C_8H_{17})_3N]Cl$	$ClCH_2CH_2Cl$	20	(70)	49[e)]	(70)	Venturello[5)]
			21[d)]	(70)			
2	$[C_6H_5CH_2(C_6H_5)_3P]_2W_2O_{11}$	$ClCH_2CH_2Cl$	4[d)]	(40)	5	(50)	Kagan[13)]
3	$[CH_3(n\text{-}C_8H_{17})_3N]_3PO_4[WO(O_2)_2]_4$[f)]	$ClCH_2CH_2Cl$	43	(70)			Venturello[11)]
			46[d)]	(70)			
4	$[R_2(CH_3)_2N]_3PO_4[WO(O_2)_2]_4$[f)] R = n-$C_{18}H_{37}$ (76%) + n-$C_{16}H_{33}$ (24%)	Benzene			66[e)]	(60)	Venturello[11)]
5	$H_3PW_{12}O_{40}$,[g)]	$CHCl_3$	17	(60)	20	(60)	Ishii[10)]
	N-hexadecylpyridinium chloride	Benzene	7	(60)			
6	$[(n\text{-}C_6H_{13})_4N]_3PO_4[WO(O_2)_2]_4$[h)]	Benzene	35	(70)	270	(70)	Griffith[8)]
			50[d)]	(70)			
7	$Na_{12}WZnMn_2(ZnW_9O_{34})_2$, $[CH_3(n\text{-}C_8H_{17})_3N]Cl$	$ClCH_2CH_2Cl$	21	(70)	<190	(70)	Neumann[15)]
		Toluene			12	(2)	
8	$Na_2WO_4 \cdot 2H_2O$, $NH_2CH_2PO_3H_2$, $[CH_3(n\text{-}C_8H_{17})_3N]HSO_4$	—	150[i)]	(60)	1600[j)]	(90)	This work
			450[d,k)]	(90)			
		Toluene	227[d,l)]	(70)	1750[m)]	(60)	
9	$[o,p\text{-}(NO_2)_2C_6H_3Se]_2$[n)]	CH_2Cl_2			19[o)]		Sharpless[20)]
10	$[o,p\text{-}(NO_2)_2C_6H_3Se]_2$, m-$ClC_6H_4CO_3H$	CH_2Cl_2			87[o,p)]		Reich[21)]
11	p-$CH_3C_6H_4AsO_3H_2$	$CHCl_3$			28[q)]	(70)	Jacobson[22)]
12	[Mn^{III}tetrakis(*o*-dichlorophenyl)porphyrin]Cl, imidazole	$CH_3CN + CH_2Cl_2$	36[r)]	(20)	36	(20)	Mansuy[12)]
13	[Mn^{III}tetrakis(*o*-dichlorophenyl)porphyrin]Cl, *N*-hexylimidazole, $C_6H_5CO_2H$	CH_2Cl_2	184[d)]	(0)	200	(0)	Banfi[14)]
14	CH_3ReO_3[s)]	t-C_4H_9OH	220[t)]	(15)	1000[u)]	(15)	Herrmann[23b)]
15	CH_3ReO_3[v)]	$CDCl_3$			97[e)]	(20)	Adam[23c)]

a) Unless otherwise stated, 30% H_2O_2 was used. b) Defined as mol product per mol transition metal atom of the catalyst. c) Reaction using 8% H_2O_2. d) Epoxidation of 1-dodecene. e) Epoxidation of cyclohexene. f) Reaction using 16% H_2O_2. g) Reaction using 35% H_2O_2. h) Reaction using 15% H_2O_2. i) Yield was 75%. j) Yield was 32%. k) Yield was 9%. l) Yield was 68%. m) Yield was 58%. n) Reaction with a large amount of $MgSO_4$. o) Defined as mol product per mol selenium atom of the catalyst. Reaction at room temperature. p) Epoxidation of cyclododecene. q) Defined as mol product per mol arsenic atom of the catalyst. r) Epoxidation of 1-nonene. s) Anhydrous H_2O_2 was used. t) Epoxidation of 1-hexene in 68% yield. u) 98% yield. v) A urea/H_2O_2 aduct was used.

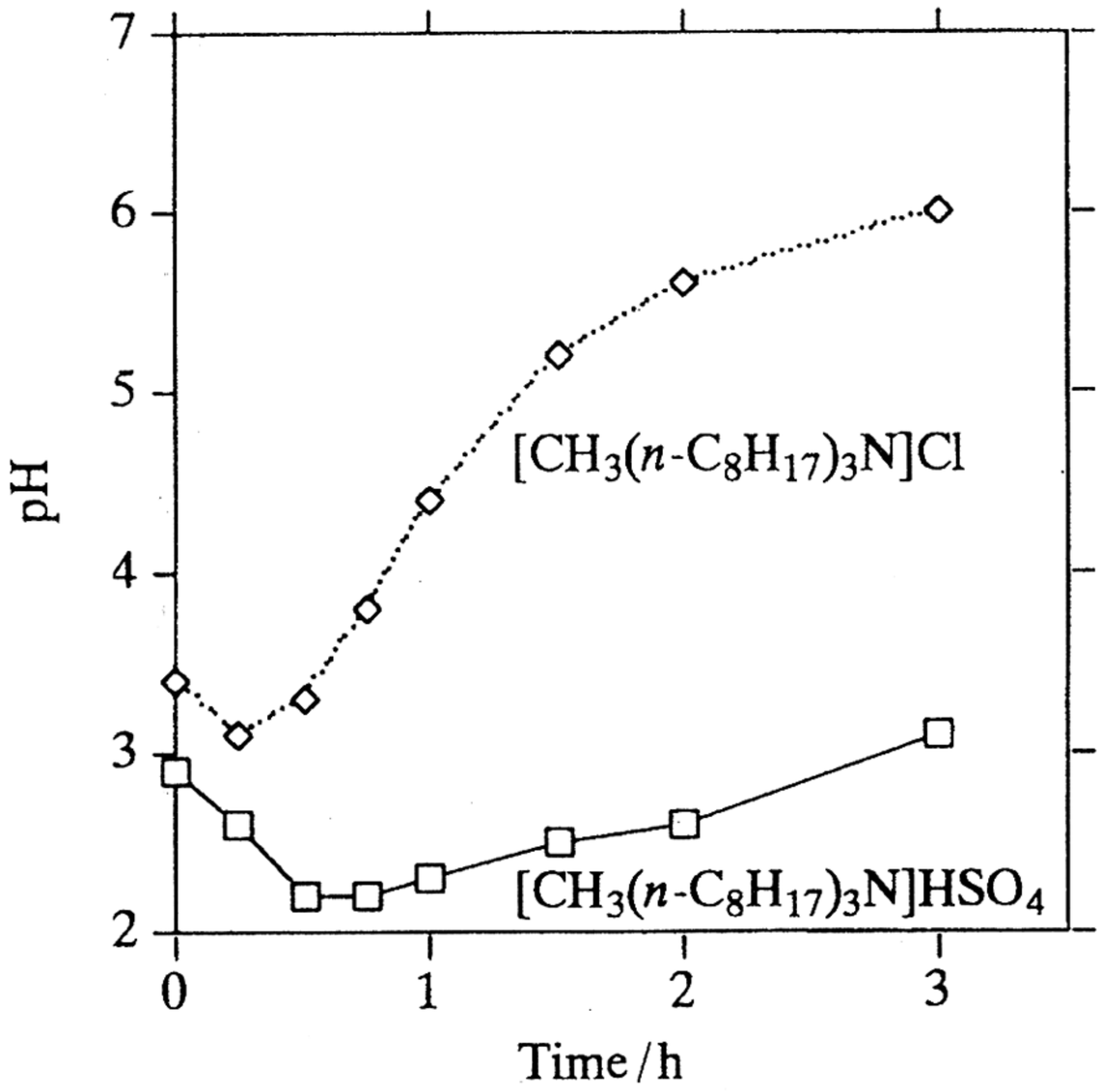


Fig. 2. Effect of the phase-transfer catalyst on pH of the water phase. Reaction was run using 30% H_2O_2, 1-octene, $Na_2WO_4 \cdot 2H_2O$, $NH_2CH_2PO_3H_2$, and phase-transfer catalyst in a 150 : 100 : 2 : 1 : 1 molar ratio at 90 °C with stirring at 1000 rpm.

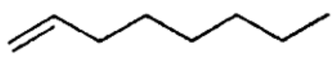
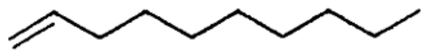
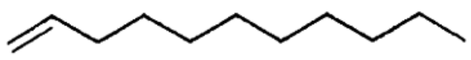
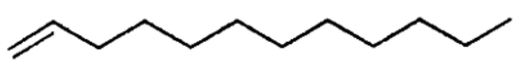
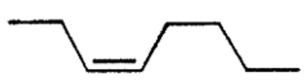
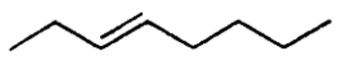
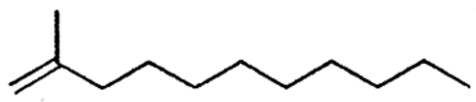
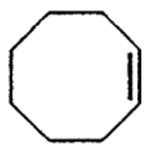
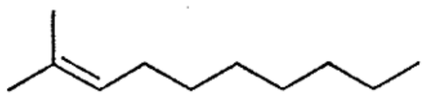
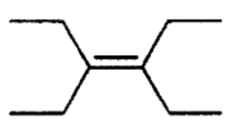
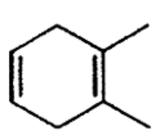
ganic solvent is faster than oxidation in toluene, owing to the higher substrate concentration. This new method is very economical; the cost of the reagents used for the oxidation of 1 mol of an olefin is only 350 yen.[19]

Although areneseleninic[20,21] or arylarsonic acids[22] act as catalysts for hydrogen peroxide epoxidation (Entries 9—11), they are much less effective than tungsten-based catalysts. The Mn(III) porphyrin–imidazole–benzoic acid combined catalyst affords a high turnover number in the epoxidation of a terminal olefin in dichloromethane, but the pH must be adjusted carefully to the 4.5—5.0 range (Entry 13). A recently developed rhenium catalyst (Entry 14) shows a turnover number as high as 1000 in the epoxidation of cyclooctene in a non-chlorocarbon solvent, but requires anhydrous hydrogen peroxide in *t*-butyl alcohol.[23]

Epoxidation of Simple Olefins. As listed in Table 4, this oxidation method finds wide applicability. Various substrates, including terminal olefins,[17] 1,1- and 1,2-disubstituted olefins, cyclic olefins, and tri- and tetrasubstituted olefins, are epoxidized in high yield with 30% hydrogen peroxide under the above-described standard conditions with or wihtout any added toluene.

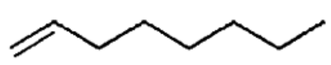
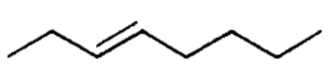
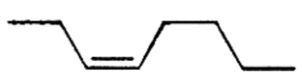
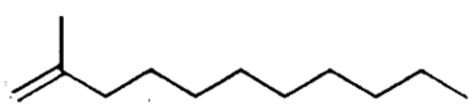
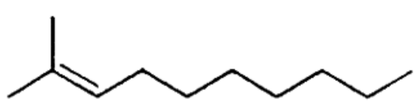
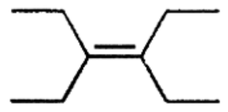
Table 5 compares the relative initial rates of the epoxida-

Table 4. Epoxidation of Olefins with 30% Hydrogen Peroxide[a]

Entry	Olefin Structure	Olefin mmol	Na_2WO_4 mmol	Toluene mL	Temp °C	Time h	Convn[b] %	Yield[b] %
1		100	2	30	90	4		81[c]
2		20	0.4	0	90	2	90	86
3		20	0.4	4	90	4	95	94
4		100	2	30	90	4		91[c]
5		20	0.4	0	90	2	92	91
6		20	0.4	4	90	4	99	99
7		594	12	0	90	2		87[c]
8		20	0.4	0	90	0.5	99	99
9		20	0.4	4	90	1	99	99
10		20	0.4	0	90	1	97	95
11		20	0.4	4	90	2	99	99
12		20	0.4	0	90	2	99	85
13		20	0.4	4	90	2	99	93
14		20	0.04	0	90	4	98	98[d]
15		20	0.4	4	40	6	93	93
16		3	0.06	0	70	1	99	99
17		3	0.06	0	70	3	93	76
18		5	0.1	1	70	1		85[e]

a) Unless otherwise stated, 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 with stirring at 1000 rpm. b) Determined by GC analysis. Based on olefin charged. c) Ref. 17. Isolated by distillation. d) H_2O_2 : olefin : Na_2WO_4 : $NH_2CH_2PO_3H_2$: $[CH_3(n\text{-}C_8H_{17})_3N]HSO_4$=150 : 100 : 2 : 1 : 0.1. e) Isolated by silica-gel column chromatography. 1,2-Epoxide : 4,5-epoxide : diepoxide=7 : 34 : 59.

Table 5. Relative Initial Rates of Epoxidation[a)]

Entry	Olefin	Relative rate[b)]
1		1
2		1.9
3		14
4		2.1
5		4.0
6		5.8

a) Reaction was run using 30% H_2O_2, 1-octene, 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 : 50 : 50 : 2 : 1 : 1 molar ratio at 90 °C with stirring at 1000 rpm. b) Determined by GC analysis. Conversion was <10%.

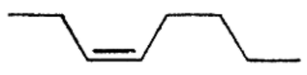
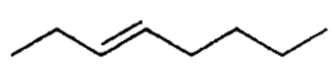
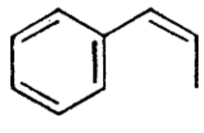
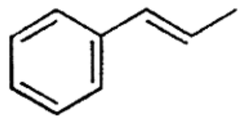
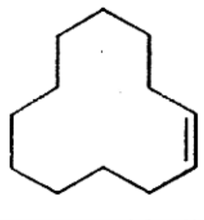
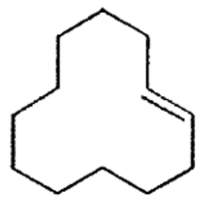
tion of simple acyclic olefins. Since the oxidizing species is electrophilic,[24)] the reaction rate is increased with increasing electron density of the olefin. However, the extent of the structural sensitivity is moderate; tetrasubstituted olefin is only 5.8-times more reactive than the terminal olefin. Notably, (Z)-3-octene is more reactive than 1-octene by a factor of 14.

The *E* and *Z* olefins give the corresponding epoxides stereospecifically with retention of the configuration. Competition experiments have revealed that this condition oxidizes the *Z* olefins preferentially over the *E* isomers. As shown in Table 6, for example, (*Z*)-3-octene is 7.3-times more reactive than the *E* isomer. The similarly high reactivity of the *Z* olefins was seen in the epoxidation using dimethyldioxirane[25)] (3-hexene, *Z* : *E*=8.3 : 1) and a special peroxycarboxylic acid[26)] (2-octene, 7.7 : 1). *m*-Chloroperbenzoic acid shows a low *Z*/*E* selectivity, 1.2 : 1. The *Z*-preference is more conspicuous with stereoisomeric β-methylstyrene, where epoxidation of the *Z* olefin occurred more than 27-times as fast as that of the *E* isomer. However, (*Z*)-cyclododecene is 4-times less reactive than the *E* isomer, presumably due to a transannular effect. 1,2-Dimethyl-1,4-cyclohexadiene is preferentially epoxidized at the less substituted C(4)–C(5) double bond, which is a 1,2-disubstituted *Z* olefinic linkage. The relative initial rate, C(4)–C(5) : C(1)–C(2)=5.3 : 1, is in contrast to epoxidation with *m*-chloroperbenzoic acid, which gives only C(1)–C(2) epoxide.[27)]

Epoxidation of Functionalized Olefins. A range of functionalized olefins can be epoxidized, although the presence of an electronegative group near to the olefinic bond reduces the nucleophilicity. Again, the reaction is accomplishable without a solvent or with added toluene. Some examples are given in Table 7. Allyl alkyl ethers (Entries 3 and 4) and an α,β-unsaturated ketone (Entry 6) gave the epoxides in a fair yield. The epoxidation of 4-oxapentadeca-1,14-diene occurred more preferentially at the C(14)–C(15) bond than at the C(1)–C(2) bond, which is close to the oxygen atom, by a factor of 2 (Entry 5). α-Ionone reacts only at the trisubstituted C=C bond in the cyclic skeleton (Entries 7 and 8).

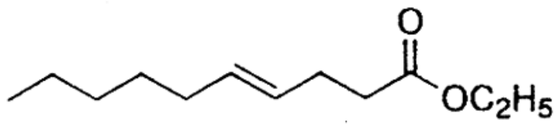
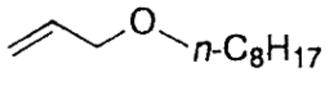
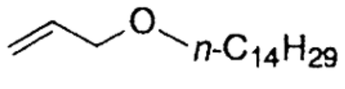
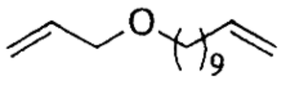
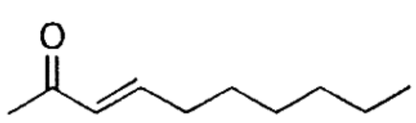
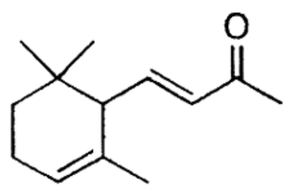
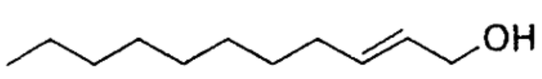
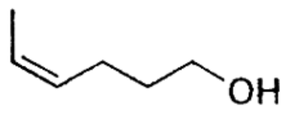
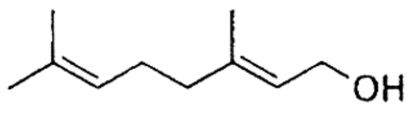
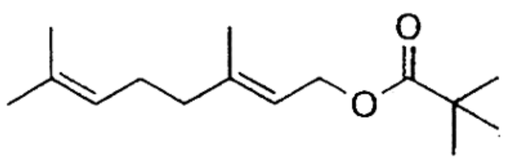
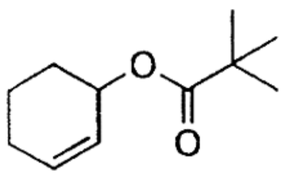
A notable exception is the reaction of allylic alcohols. In spite of the presence of an electronegative hydroxy group, allylic alcohols react much faster than do simple olefins. The hydroxy group facilitates the reaction, and also directs the stereochemical outcome. Thus, geraniol underwent a reaction smoothly even at 0 °C to form only C(2)–C(3) epoxide (Entry 12). In contrast, the reaction of the pivalate required heating at 60 °C and epoxidized mainly the C(6)–C(7) position (Entry 13). The initial relative selectivity was C(6)–C(7) : C(2)–C(3)=ca. 3.2 : 1. The epoxidation of 2-cyclohexen-1-ol occurred stereoselectively from the face of the hydroxy function (*syn* : *anti*=9 : 1), while the pivalate exhibited an opposite diastereoselection (*syn* : *anti*=1 : 12) (Table 8). Competition experiments revealed that the relative reactivity of 2-cyclohexen-1-ol, cyclohexene, and pivalate of 2-cyclohexen-1-ol is 170 : 1 : 0.05. The epoxidation of 2-cyclohexen-1-ol by *m*-chloroperbenzoic acid exhibits a similar syn selectivity,[28)] whereas the hydroxy function tends to decelerate the electrophilic epoxidation. *m*-Chloroperbenzoic acid showed little diastereoselectivity in the pivalate epoxi-

Table 6. Relative Rates of Epoxidation

Entry	Olefins			Relative *Z*/*E* rates[a)]	
				This method[b)]	*m*-$ClC_6H_4CO_3H$
1		and		7.3	1.2
2		and		>27	0.84
3		and		0.27	0.47

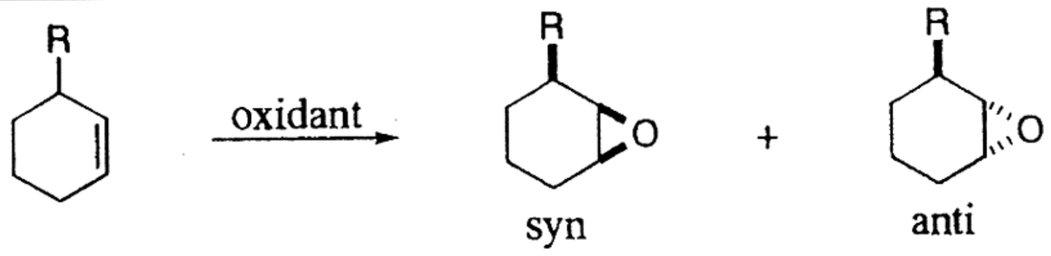
a) Determined by GC analysis. Conversion was <10%. b) Reaction was run using 30% H_2O_2, (*E*)-olefin, (*Z*)-olefin, $Na_2WO_4 \cdot 2H_2O$, $NH_2CH_2PO_3H_2$, and $[CH_3(n\text{-}C_8H_{17})_3N]HSO_4$ in a 150 : 50 : 50 : 2 : 1 : 1 molar ratio at 70 °C with stirring at 1000 rpm.

Table 7. Epoxidation of Functionalized Olefins with 30% Hydrogen Peroxide[a)]

Entry	Olefin Structure	Olefin mmol	Na_2WO_4 mmol	Toluene mL	Temp °C	Time h	Convn[b)] %	Yield[b)] %
1		20	0.4	0	90	2	99	88
2		20	0.4	4	90	2	99	99
3		20	0.4	4	100	2	81	64
4		20	0.4	4	90	2	77	75
5		5	0.1	2	70	2		42[c,d)]
6		20	0.4	4	90	5.5	61	61
7		20	0.4	0	90	1	92	77[e)]
8		20	0.4	4	90	1	99	91[e)]
9		20	0.4	0	90	0.17	88	73
10		20	0.4	4	90	0.5	86	86
11		20	0.4	4	90	5.5	61	61
12		20	0.4	0	0	2		82[c,f)]
13		20	0.4	0	60	1		85[c,g)]
14		20	0.4	0	60	2		72[c,h)]

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 with stirring at 1000 rpm. b) Determined by GC analysis. Based on olefin charged. c) Isolated by silica-gel column chromatography. d) 1,2-Epoxide : 14,15-epoxide : diepoxide=26 : 62 : 12. e) Epoxide of the cyclic olefin. f) Pure 2,3-epoxide. g) 6,7-Epoxide : diepoxide=44 : 56. h) *r*-1,*c*-2,*c*-3-Epoxide : *r*-1,*t*-2,*t*-3-epoxide=8 : 92.

Table 8. Relative Rates and Stereoselectivity in Epoxidation of 3-Substituted Cyclohexenes



Entry	R	Relative rates (*syn*/*anti*[a)]) This method[b,c)]	Relative rates (*syn*/*anti*[a)]) *m*-$ClC_6H_4CO_3H$
1	H	1	1
2	OH	>170 (90/10)[d)]	0.55 (92/8)[e)]
3	$OCOCH_3$	0.20 (11/89)	0.046 (37/63)[e)]
4	$OCOC(CH_3)_3$	0.05 (8/92)	— (45/55)[c)]

a) For epoxycyclohexanol derivatives, *syn*=*r*-1,*c*-2,*c*-3 and *anti*=*r*-1,*t*-2,*t*-3. b) Reaction was run using 30% H_2O_2, cyclohexene, 3-substituted cyclohexene, $Na_2WO_4 \cdot 2H_2O$, $NH_2CH_2PO_3H_2$, and $[CH_3(n\text{-}C_8H_{17})_3N]HSO_4$ in a 150 : 50 : 50 : 2 : 1 : 1 molar ratio at 50 °C with stirring at 1000 rpm. b) Determined by GC analysis. Conversion was <10%. d) Reaction was run at room temperature. e) Ref. 28.

dation (*syn* : *anti*=1 : 1.2).

Limitation. With simple aliphatic olefins used as substrates, the conversion of the substrate is close to the yield of the epoxy product, where the difference is ascribed to the formation of by-products. The difficulty encountered in the epoxidation of styrene and the simple derivatives is shown in Table 9. The reaction of unsubstituted styrene at 70 °C for 3 h with stirring at 1000 rpm gave 2-phenyloxirane in only a 2% yield at 70% conversion (Entry 3). This discouraging result was due to the hydrolytic decomposition of the acid-sensitive epoxide that probably occurs at the aqueous/organic interface. The undesired reaction was reduced by increasing the volume of toluene and decreasing the stirring rate from 1000 to 250 rpm. The yield was thus increased to 23%, though still unsatisfactory (Entry 2). Notably, the epoxide yield was increased from this value to 65 and 69% along with an increase in the lipophilicity[29)] from 2-phenyloxirane (log *P*=1.1) to the *p*-*t*-butyl derivative (3.9) and the *p*-nonyl compound (7.2), respectively (Entries 4 and 5). Both the acid sensitivity and the lipophilicity of the epoxide product must

Table 9. Epoxidation of Styrene Derivatives, p-$RC_6H_4CH{=}CH_2$[a]

	Olefin		Na_2WO_4	Toluene	Stirring rate	Temp	Time	Convn[b]	Product	
Entry	R	mmol	mmol	mL	rpm	°C	h	%	Yield[b]/%	log P
1	H	20	0.4	10	1000	70	3	52	3	1.1
2	H	20	0.4	10	250	70	1	34	23	1.1
3	H	20	0.4	4	1000	70	3	70	2	1.1
4	t-C_4H_9	20	0.4	10	250	70	4	81	65	3.9
5	n-C_9H_{19}	5	0.1	2.5	1000	90	2	72	69	7.2

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. b) Determined by GC analysis. Based on olefin charged.

be taken into account in selecting the conditions of the biphasic epoxidation. Another problem is the oxidation of olefinic alcohols having a high reduction potential.[30] 2-Octanol was found to be 4.6-times more reactive than 1-octene. 1-Octanol was oxidized, first giving octanal, and then octanoic acid, at a rate similar to that of 1-octene. The hydroxy groups in the allylic alcohols and their epoxides were not affected under the olefin epoxidation conditions.

Conclusion

A system consisting of sodium tungstate dihydrate, (aminomethyl)phosphonic acid, and methyltrioctylammonium hydrogensulfate in a 2 : 1 : 1 molar ratio acts as a highly active catalyst for olefin epoxidation with aqueous 30% hydrogen peroxide under entirely halide-free conditions. The use of a lipophilic ammonium hydrogensulfate and an (α-aminoalkyl)phosphonic acid is significant for achieving high reactivity. The biphasic epoxidation of simple olefins can be carried out at 40—90 °C with a substrate-to-catalyst ratio of 50—500 without organic solvents or by adding toluene. The reaction of cyclic olefins and allylic alcohols proceeds with a smaller amount of the catalyst and under milder conditions. The reaction sometimes exhibits a unique selectivity profile unobservable with the conventional epoxidation methods. This practical epoxidation can be conducted safely and economically on a large scale under environmentally benign conditions.

Experimental

General. ^{1}H NMR spectra were recorded on a JEOL JNM-A400 NMR spectrometer at 400 MHz. The chemical shifts are reported in ppm on the δ scale downfield from tetramethylsilane used as an internal standard; and signal patterns are indicated as follows: s, singlet; d, doublet; t, triplet; q, quartet; 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 (77.00 ppm) as an internal standard. Gas chromatographic (GC) analyses were performed on a Shimadzu GC-14A gas chromatograph using an OV-1 column (0.25 mm×50 m, GL Sciences Inc.) and helium (1.2 kg cm^{-2}) as a carrier gas, unless otherwise stated.

Materials. Sodium tungstate dihydrate, aqueous 30% hydrogen peroxide, phosphoric acid, phenylphosphonic acid, dimethyl sulfate, trioctylamine, N-hexadecylpyridinium chloride, tetrabutylammonium chloride, tetrabutylammonium hydrogensulfate, and toluene were obtained from Nacalai Tesque, Inc., and used as received. 1-Octene, 1-nonene, 1-undecene, 1-dodecene, (Z)-3-octene, (E)-3-octene, 2-methyl-1-undecene, cyclohexene, cyclooctene, cyclododecene, styrene, (Z)-β-methylstyrene, (E)-β-methylstyrene, ethyl(E)-4-decenoate, 4-oxadodec-1-ene, 3-decen-2-one, (Z)-4-hexen-1-ol, (E)-2-undecen-1-ol, (E)-4-(2,6,6-trimethyl-2-cyclohexen-1-yl)-3-buten-2-one, 1-octanol, 2-octanol, geraniol, and 2-cyclohexen-1-ol were purchased from Tokyo Kasei Kogyo Co., Ltd., and were distilled before use. Tetrakis(decyl)ammonium hydroxide, tetraoctylammonium hydroxide, methyltrioctylammonium chloride, tetrahexylammonium hydroxide, tetrabutylammonium hydroxide, and benzyltriethylammonium hydroxide were obtained from Tokyo Kasei Kogyo Co., Ltd., and used as received. Tetrakis(decyl)ammonium hydrogensulfate and tetrahexylammonium hydrogensulfate were prepared from sulfuric acid and the corresponding ammonium hydroxide. Trialkylmethylammonium hydrogensulfate containing C_6 to C_{10} alkyl chains was prepared from sulfuric acid and trialkylmethylammonium chloride, which was obtained from Tokyo Kasei Kogyo Co., Ltd. Methyltrioctylammonium sulfate was synthesized from methyltrioctylammonium chloride and sodium sulfate. A convenient method for preparing methyltrioctylammonium hydrogensulfate is given in Ref. 17. 1-Decene and p-t-butylstyrene were purchased from Aldrich Chemical Co. and purified by distillation before use. (Aminomethyl)phosphonic acid,[31] (2-aminoethyl)phosphonic acid,[32] (3-aminopropyl)phosphonic acid,[32] 1,2-dimethyl-1,4-cyclohexadiene,[27] and p-nonylstyrene[33] were synthesized according to the literature. 3,4-Diethyl-3-hexene was prepared from the reductive coupling[34] of 3-pentanone. 4-Oxaoctadec-1-ene was prepared from allyl chloride and 1-tetradecanol in the presence of sodium hydride. 4-Oxapentadeca-1,14-diene was obtained by the allylation of 10-undecen-1-ol. 2-Methyl-2-decene was prepared by the Witting reaction. 2-Cyclohexen-1-yl acetate was prepared from acetyl chloride and 2-cyclohexen-1-ol in the presence of pyridine. Pivalate of geraniol and pivalate of 2-cyclohexen-1-ol were prepared from pivaloyl chloride and the corresponding alcohols.

General Procedure for Epoxidation. A 20-mL, round-bottomed flask equipped with a magnetic stirring bar and a reflux condenser was charged with 131.9 mg (0.40 mmol) of $Na_2WO_4{\cdot}2H_2O$, 22.2 mg (0.20 mmol) of $NH_2CH_2PO_3H_2$, 3.40 g (30 mmol) of aqueous 30% H_2O_2, and 93.2 mg (0.20 mmol) of $[CH_3(n\text{-}C_8H_{17})_3N]HSO_4$. After the mixture was vigorously stirred at room temperature for 15 min, 20 mmol of olefin (near or in toluene) was added. This mixture was heated and stirred at 1000 rpm. The reaction temperatures and times are indicated in Tables 4, 7, and 9. After cooling to room temperature, the organic phase was separated, washed with 5 mL of saturated aqueous $Na_2S_2O_3$, and distilled through a short column under a vacuum to give the pure epoxide.

The conversion and yield were determined by running the reaction with 4 mmol of internal standard, typically nonane. The disappearance of the substrate (conversion) and the formation of

the epoxy product (yield) were monitored by GC analysis of small aliquots of the organic phase. The GC data were corrected for the relative response of the detector by integrating the response of each analyte against an internal standard.

A procedure for the hectogram-scale epoxidation of 1-dodecene is described in Ref. 17.

General Procedure for Relative Rate Study. A 10-mL, round-bottomed flask equipped with a magnetic stirring bar and a reflux condenser was charged with 66.0 mg (0.20 mmol) of $Na_2WO_4 \cdot 2H_2O$, 11.1 mg (0.10 mmol) of $NH_2CH_2PO_3H_2$, 1.70 g (15 mmol) of aqueous 30% H_2O_2, and 46.6 mg (0.10 mmol) of $[CH_3(n\text{-}C_8H_{17})_3N]HSO_4$. After the mixture was stirred at 1000 rpm at room temperature for 15 min, a mixture of each 5 mmol of the substrates and 1 mmol of the internal standard (typically nonane) was added. This mixture was heated to 90 °C (Table 5 and competitive reactions of 1- or 2-octanol to 1-octene), 70 °C (Table 6), or 50 °C (Table 8). The disappearance of the substrates was monitored at low conversion after stirring at 1000 rpm for 5—10 min in order to ensure that the concentration of oxidant did not change appreciably during the reaction. The GC data were corrected by integrating the response of each analyte against an internal standard.

1,2-Epoxynonane.[35] GC; initial column temp, 70 °C; final column temp, 280 °C; progress rate, 5 °C min^{-1}; injection temp, 280 °C; split ratio, 100 : 1; reaction time (t_R) of 1-nonene, 8.4 min; t_R of 1,2-epoxynonane, 14.1 min. ^1H NMR (400 MHz, $CDCl_3$) δ=0.88 (t, 3H, J=7.2 Hz), 1.28—1.53 (m, 12H), 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=14.10, 22.67, 26.01, 29.26, 29.44, 31.80, 32.53, 47.12, 52.40.

1,2-Epoxyundecane. GC; initial column temp, 70 °C; final column temp, 280 °C; progress rate, 9 °C min^{-1}; injection temp, 280 °C; split ratio, 100 : 1; t_R of 1-undecene, 10.5 min; t_R of 1,2-epoxyundecane, 14.5 min. Found: C, 77.57; H, 13.05%. Calcd for $C_{11}H_{22}O$: C, 77.58; H, 13.02%. ^1H NMR (400 MHz, $CDCl_3$) δ=0.88 (t, 3H, J=6.8 Hz), 1.27—1.54 (m, 16H), 2.46 (dd, 1H, J=3.0, 4.9 Hz), 2.74 (dd, 1H, J=4.0, 4.9 Hz), 2.90 (br, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ=14.16, 22.73, 26.04, 29.36, 29.51, 29.58, 29.63, 31.95, 32.57, 47.16, 52.44.

***cis*-2-Butyl-3-ethyloxirane.** GC; initial column temp, 70 °C; final column temp, 280 °C; progress rate, 5 °C min^{-1}; injection temp, 280 °C; split ratio, 100 : 1; t_R of (*Z*)-3-octene, 7.4 min; t_R of *cis*-2-butyl-3-ethyloxirane, 10.1 min. Found: C, 74.86; H, 12.77%. Calcd for $C_8H_{16}O$: C, 74.94; H, 12.58%. ^1H NMR (400 MHz, $CDCl_3$) δ=0.93 (t, 3H, J=7.0 Hz), 1.04 (t, 3H, J=7.6 Hz), 1.37—1.61 (m, 8H), 2.85—2.93 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ=10.56, 13.97, 21.07, 22.60, 27.37, 28.71, 57.31, 58.34.

***trans*-2-Butyl-3-ethyloxirane.** GC; initial column temp, 70 °C; final column temp, 280 °C; progress rate, 5 °C min^{-1}; injection temp, 280 °C; split ratio, 100 : 1; t_R of (*E*)-3-octene, 7.5 min; t_R of *trans*-2-butyl-3-ethyloxirane, 9.8 min. Found: C, 74.93; H, 12.72%. Calcd for $C_8H_{16}O$: C, 74.94; H, 12.58%. ^1H NMR (400 MHz, $CDCl_3$) δ=0.91 (t, 3H, J=6.8 Hz), 0.99 (t, 3H, J=7.2 Hz), 1.37—1.59 (m, 8H), 2.63—2.67 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ=9.87, 13.94, 22.46, 25.15, 28.15, 31.76, 58.58, 59.91.

2-Methyl-1,2-epoxyundecane. GC; initial column temp, 70 °C; final column temp, 280 °C; progress rate, 10 °C min^{-1}; injection temp, 280 °C; split ratio, 100 : 1; t_R of 2-methyl-1-undecene, 11.7 min; t_R of 2-methyl-1,2-epoxyundecane, 14.4 min. Found: C, 78.20; H, 13.34%. Calcd for $C_{12}H_{24}O$: C, 78.20; H, 13.12%. ^1H NMR (400 MHz, $CDCl_3$) δ=0.88 (t, 3H, J=6.8 Hz), 1.27—1.57 (m, 19H), 2.55 (d, 1H, J=5.0 Hz), 2.59 (d, 1H, J=5.0 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ=14.00, 20.81, 22.60, 25.19, 29.24, 29.46, 29.51, 29.61, 31.82, 36.70, 53.79, 56.91.

1,2-Epoxycyclooctane. The reaction was run in a manner identical with the General Procedure for Epoxidation, except that 13.2 mg (0.04 mmol) of $Na_2WO_4 \cdot 2H_2O$, 2.2 mg (0.02 mmol) of $NH_2CH_2PO_3H_2$, and 9.3 mg (0.02 mmol) of $[CH_3(n\text{-}C_8H_{17})_3N]HSO_4$ were used. GC; initial column temp, 70 °C; final column temp, 280 °C; progress rate, 5 °C min^{-1}; injection temp, 280 °C; split ratio, 100 : 1; t_R of cyclooctene, 7.3 min; t_R of 1,2-epoxycyclooctane, 11.5 min. Found: C, 76.08; H, 11.42%. Calcd for $C_8H_{14}O$: C, 76.14; H, 11.18%. ^1H NMR (400 MHz, $CDCl_3$) δ=1.22—1.33 (m, 2H), 1.42—1.66 (m, 8H), 2.12—2.17 (m, 2H), 2.87—2.92 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ=25.51, 26.21, 26.47, 55.54.

2-Methyl-2,3-epoxydecane.[36] The reaction was performed by using a 10-mL flask, 19.8 mg (0.06 mmol) of $Na_2WO_4 \cdot 2H_2O$, 3.3 mg (0.03 mmol) of $NH_2CH_2PO_3H_2$, 510 mg (4.5 mmol) of aqueous 30% H_2O_2, 14.0 mg (0.03 mmol) of $[CH_3(n\text{-}C_8H_{17})_3N]HSO_4$, and 462.9 mg (3.0 mmol) of 2-methyl-2-decene. GC; initial column temp, 70 °C; final column temp, 280 °C; progress rate, 10 °C min^{-1}; injection temp, 280 °C; split ratio, 100 : 1; t_R of 2-methyl-2-decene, 10.9 min; t_R of 2-methyl-2,3-epoxydecane, 12.6 min. ^1H NMR (400 MHz, $CDCl_3$) δ=0.89 (t, 3H, J=6.8 Hz), 1.26—1.57 (m, 18H), 2.71 (t, 1H, J=5.6 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ=14.00, 18.65, 22.58, 24.84, 26.47, 28.80, 29.19, 29.41, 31.72, 58.07, 64.48.

3,4-Diethyl-3,4-epoxyhexane.[37] The product was obtained by a reaction using a 10-mL flask, 19.8 mg (0.06 mmol) of $Na_2WO_4 \cdot 2H_2O$, 3.3 mg (0.03 mmol) of $NH_2CH_2PO_3H_2$, 510 mg (4.5 mmol) of aqueous 30% H_2O_2, 14.0 mg (0.03 mmol) of $[CH_3(n\text{-}C_8H_{17})_3N]HSO_4$, and 420.8 mg (3.0 mmol) of 3,4-diethyl-3-hexene. GC; initial column temp, 70 °C; final column temp, 280 °C; progress rate, 10 °C min^{-1}; injection temp, 280 °C; split ratio, 100 : 1; t_R of 3,4-diethyl-3-hexene, 8.6 min; t_R of 3,4-diethyl-3,4-epoxyhexane, 10.1 min. ^1H NMR (400 MHz, $CDCl_3$) δ=0.95 (t, 12H, J=7.3 Hz), 1.46—1.57 (m, 4H), 1.62—1.73 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ=9.37, 22.98, 69.62.

Epoxidation of 1,2-Dimethyl-1,4-cyclohexadiene. A 10-mL flask was charged with 33.0 mg (0.10 mmol) of $Na_2WO_4 \cdot 2H_2O$, 5.6 mg (0.05 mmol) of $NH_2CH_2PO_3H_2$, 800 mg (7.5 mmol) of aqueous 30% H_2O_2, and 23.3 mg (0.05 mmol) of $[CH_3(n\text{-}C_8H_{17})_3N]HSO_4$. After the mixture was vigorously stirred at room temperature for 20 min, 540.9 mg (5.0 mmol) of 1,2-dimethyl-1,4-cyclohexadiene and 1 mL of toluene were added. This mixture was heated at 70 °C for 1 h with stirring at 1000 rpm. The organic phase was separated, washed with 5 mL of saturated aqueous $Na_2S_2O_3$, and chromatographed on silica gel (BW 300, 100 g; eluent, 3 : 1 hexane–ether) to give 36.9 mg (6%) of 4,5-dimethyl-4,5-epoxycyclohexene, 179.4 mg (29%) of 1,2-dimethyl-4,5-epoxycyclohexene, and 351.5 mg (50%) of 1,2-dimethyl-1,2 : 4,5-diepoxycyclohexane as a colorless liquid.

4,5-Dimethyl-4,5-epoxycyclohexene: Found: C, 77.38; H, 9.96%. Calcd for $C_8H_{12}O$: C, 77.38; H, 9.74%. ^1H NMR (400 MHz, $CDCl_3$) δ=1.36 (s, 6H), 2.30—2.50 (m, 4H), 5.43 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ=19.69, 32.10, 61.09, 122.82.

1,2-Dimethyl-4,5-epoxycyclohexene: Found: C, 77.38; H, 9.95%. Calcd for $C_8H_{12}O$: C, 77.38; H, 9.74%. ^1H NMR (400 MHz, $CDCl_3$) δ=1.59 (s, 6H), 2.26—2.48 (m, 4H), 3.25 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ=18.85, 31.40, 51.66, 120.19.

1,2-Dimethyl-1,2 : 4,5-diepoxycyclohexane: Found: C, 68.53; H, 8.76%. Calcd for $C_8H_{12}O_2$: C, 68.55; H, 8.63%. ^1H NMR (400 MHz, $CDCl_3$) δ=1.31 (s, 6H), 2.14 (d, 2H, J=16.8 Hz), 2.31 (dd, 2H, J=3.3, 16.8 Hz), 3.05 (d, 2H, J=3.3 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ=20.08, 31.00, 50.02, 59.29.

Ethyl 3-(*trans*-3-Pentyl-2-oxiranyl)propanoate. GC; initial

column temp, 80 °C; final column temp, 280 °C; progress rate, 10 °C min^{-1}; injection temp, 280 °C; split ratio, 100 : 1; t_R of ethyl(*E*)-4-decenoate, 13.7 min; t_R of ethyl-3-(*trans*-3-pentyl-2-oxiranyl)-propanoate, 16.0 min. Found: C, 67.18; H, 10.72%. Calcd for $C_{12}H_{20}O_3$: C, 67.26; H, 10.35%. ^{1}H NMR (400 MHz, $CDCl_3$) δ=0.89 (t, 3H, J=6.8 Hz), 1.26 (t, 3H, J=6.8 Hz), 1.29—1.55 (m, 8H), 1.72—1.81 (m, 1H). 1.91—1.99 (m, 1H), 2.44 (dt, 2H, J=1.6, 7.2 Hz), 2.68—2.75 (m, 2H), 4.14 (q, 2H, J=6.8 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ=13.90, 14.13, 22.49, 25.57, 27.27, 30.47, 31.53, 31.86, 57.47, 58.85, 60.40, 172.82.

1,2-Epoxy-4-oxadodecane. This epoxide was obtained by a reaction using 4-oxadodec-1-ene in 4 mL of toluene. GC; initial column temp, 80 °C; final column temp, 280 °C; progress rate, 10 °C min^{-1}; injection temp, 280 °C; split ratio, 100 : 1; t_R of 4-oxadodec-1-ene, 10.8 min; t_R of 1,2-epoxy-4-oxadodecane, 13.9 min. Found: C, 70.91; H, 12.17%. Calcd for $C_{11}H_{22}O_2$: C, 70.92; H, 11.90%. ^{1}H NMR (400 MHz, $CDCl_3$) δ=0.88 (t, 3H, J=6.8 Hz), 1.27 (br, 10H), 1.58 (q, 2H, J=6.8 Hz), 2.60 (dd, 1H, J=2.8, 4.9 Hz), 2.78 (dd, 1H, J=3.6, 4.9 Hz), 3.12—3.16 (m, 1H), 3.38 (dd, 1H, J=6.0, 11.2 Hz), 3.43—3.54 (m, 2H), 3.70 (dd, 1H, J=3.6, 11.2 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ=13.96, 22.53, 25.97, 29.14, 29.32, 29.59, 31.70, 44.15, 50.76, 71.34, 71.59.

1,2-Epoxy-4-oxaoctadecane. The reaction was run using 4-oxaoctadec-1-ene in 4 mL of toluene. GC; initial column temp, 80 °C; final column temp, 280 °C; progress rate, 10 °C min^{-1}; injection temp, 280 °C; split ratio, 100 : 1; t_R of 4-oxaoctadec-1-ene, 18.2 min; t_R of 1,2-epoxy-4-oxaoctadecane, 21.2 min. Found: C, 75.43; H, 12.97%. Calcd for $C_{17}H_{34}O_2$: C, 75.50; H, 12.67%. ^{1}H NMR (400 MHz, $CDCl_3$) δ=0.88 (t, 3H, J=6.8 Hz), 1.27 (br, 22H), 1.56—1.62 (m, 2H), 2.61 (dd, 1H, J=2.8, 4.9 Hz), 2.80 (dd, 1H, J=3.6, 4.9 Hz), 3.13—3.17 (m, 1H), 3.39 (dd, 1H, J=6.0, 11.2 Hz), 3.43—3.54 (m, 2H), 3.70 (dd, 1H, J=3.6, 11.2 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ=14.08, 22.66, 26.06, 29.33, 29.45, 29.56, 29.59, 29.62, 29.64, 29.65, 29.68, 31.90, 44.31, 50.88, 71.43, 71.71.

Epoxidation of 4-Oxapentadeca-1,14-diene. A mixture of 33.0 mg (0.10 mmol) of $Na_2WO_4 \cdot 2H_2O$, 5.6 mg (0.05 mmol) of $NH_2CH_2PO_3H_2$, 570 mg (5.0 mmol) of aqueous 30% H_2O_2, and 23.3 mg (0.05 mmol) of $[CH_3(n\text{-}C_8H_{17})_3N]HSO_4$ was vigorously stirred at room temperature for 20 min. Then, 1.052 g (5.0 mmol) of 4-oxapentadeca-1,14-diene and 2 mL of toluene were added, and the mixture was heated at 70 °C for 2 h with stirring at 1000 rpm. The organic phase was separated, washed with 5 mL of saturated aqueous $Na_2S_2O_3$, and chromatographed on silica gel (BW 300, 150 g; eluent, 10 : 1 hexane–ether) to give 123.6 mg (11%) of 1,2-epoxy-4-oxapentadec-14-ene, 294.7 mg (26%) of 14,15-epoxy-4-oxapentadec-1-ene, and 61.1 mg (5%) of 1,2 : 14,15-diepoxy-4-oxapentadecane as a colorless liquid.

1,2-Epoxy-4-oxapentadec-14-ene: Found: C, 74.06; H, 11.72%. Calcd for $C_{14}H_{26}O_2$: C, 74.29; H, 11.58%. ^{1}H NMR (400 MHz, $CDCl_3$) δ=1.28—1.37 (m, 12H), 1.52—1.63 (m, 2H), 2.01—2.06 (m, 2H), 2.60 (dd, 2H, J=2.8, 5.2 Hz), 2.79 (dd, 2H, J=4.0, 5.2 Hz), 3.12—3.16 (m, 1H), 3.38 (dd, 1H, J=6.0, 11.6 Hz), 3.43—3.54 (m, 2H), 3.70 (dd, 1H, J=2.8, 11.6 Hz), 4.93 (dd, 1H, J=2.4, 10.0 Hz), 4.99 (dd, 1H, J=2.4, 16.8 Hz), 5.81 (ddt, 1H, J=6.4, 10.0, 16.8 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ=26.03, 28.88, 29.07, 29.37, 29.40, 29.47, 29.65, 33.76, 44.28, 50.85, 71.42, 71.67, 114.05, 139.17.

14,15-Epoxy-4-oxapentadec-1-ene: Found: C, 74.28; H, 11.93%. Calcd for $C_{14}H_{26}O_2$: C, 74.29; H, 11.58%. ^{1}H NMR (400 MHz, $CDCl_3$) δ=1.30—1.60 (m, 16H), 2.45 (dd, 1H, J=2.9, 4.8 Hz), 2.74 (t, 1H, J=4.8 Hz), 2.88—2.92 (m, 1H), 3.42 (t, 2H, J=6.4 Hz), 3.96 (d, 2H, J=5.2 Hz), 5.16 (dd, 1H, J=1.6, 10.4 Hz), 5.26 (dd, 1H, J=1.6, 17.2 Hz), 5.92 (ddt, 1H, J=5.2, 10.4, 17.2 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ=25.90, 26.12, 29.36, 29.39, 29.41, 29.42, 29.71, 32.43, 47.04, 52.32, 70.44, 71.73, 116.57, 135.07.

1,2 : 14,15-Diepoxy-4-oxapentadecane: Found: C, 69.16; H, 10.82%. Calcd for $C_{14}H_{26}O_3$: C, 69.38; H, 10.81%. ^{1}H NMR (400 MHz, $CDCl_3$) δ=1.30—1.60 (m, 16H), 2.46 (dd, 1H, J=2.8, 5.2 Hz), 2.60 (dd, 1H, J=2.8, 5.2 Hz), 2.74 (dd, 1H, J=4.0, 5.2 Hz), 2.80 (dd, 1H, J=4.0, 5.2 Hz), 2.88—2.91 (m, 1H), 3.13—3.16 (m, 1H), 3.38 (dd, 1H, J=5.6, 11.6 Hz), 3.45—3.52 (m, 2H), 3.71 (dd, 1H, J=2.8, 11.6 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ=25.92, 26.02, 29.38, 29.41, 29.42, 29.43, 29.65, 32.44, 44.29, 47.08, 50.87, 52.35, 71.43, 71.66.

3,4-Epoxy-2-decanone. The product was obtained by epoxidation using 3-decen-2-one in 4 mL of toluene. GC; initial column temp, 80 °C; final column temp, 280 °C; progress rate, 10 °C min^{-1}; injection temp, 280 °C; split ratio, 100 : 1; t_R of 3-decen-2-one, 11.5 min; t_R of 3,4-epoxy-2-decanone, 12.2 min. Found: C, 70.55; H, 10.89%. Calcd for $C_{10}H_{18}O_2$: C, 70.55; H, 10.66%. ^{1}H NMR (400 MHz, $CDCl_3$) δ=0.89 (t, 3H, J=6.8 Hz), 1.29—1.38 (m, 6H), 1.44—1.51 (m, 2H), 1.57—1.68 (m, 2H), 2.06 (s, 3H), 3.08 (dt, 1H, J=2.0, 5.6 Hz), 3.18 (d, 1H, J=2.0 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ=13.92, 22.41, 24.24, 25.64, 28.81, 31.54, 31.68, 57.99, 59.83, 205.98.

(*E*-4-(2,6,6-Trimethyl-2,3-epoxycyclohexyl)-3-buten-2-one.[36] GC; initial column temp, 80 °C; final column temp, 280 °C; progress rate, 10 °C min^{-1}; injection temp, 280 °C; split ratio, 100 : 1; t_R of (*E*)-4-(2,6,6-trimethyl-2-cyclohexyl)-3-buten-2-one, 14.5 min; t_R of (*E*)-4-(2,6,6-trimethyl-2,3-epoxycyclohexyl)-3-buten-2-one, 16.2 min. ^{1}H NMR (400 MHz, $CDCl_3$) δ=0.75 (d, 3H, J=1.6 Hz), 0.93 (d, 3H, J=2.0 Hz), 1.03 (br, 1H), 1.26 (d, 3H, J=1.6 Hz), 1.42 (br, 1H), 1.91 (br, 1H), 1.99 (br, 1H), 2.09 (d, 1H, J=10.0 Hz), 2.30 (s, 3H), 3.10 (s, 1H), 6.10 (d, 1H, J=16.0 Hz), 6.71 (dd, 1H, J=10.0, 16.0 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ=21.67, 23.97, 26.37, 27.43, 27.80, 28.41, 31.13, 52.38, 58.70, 59.40, 133.96, 146.31, 198.69.

***trans*-3-Octyloxiranemethanol.**[38] GC; initial column temp, 80 °C; final column temp, 280 °C; progress rate, 10 °C min^{-1}; injection temp, 280 °C; split ratio, 100 : 1; t_R of (*E*)-2-undecen-1-ol, 15.2 min; t_R of *trans*-3-octyloxiranemethanol, 17.5 min. ^{1}H NMR (400 MHz, $CDCl_3$) δ=0.88 (t, 3H, J=6.8 Hz), 1.27 (br, 10H), 1.37—1.63 (m, 4H), 1.68 (br, 1H), 2.91—2.97 (m, 2H), 3.63 (d, 1H, J=12.4 Hz), 3.92 (d, 1H, J=12.4 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ=14.06, 22.62, 25.92, 29.18, 29.37, 29.46, 31.53, 31.81, 56.01, 58.47, 61.71.

***cis*-3-Methyloxiranepropanol.** The reaction using (*Z*)-4-hexen-1-ol in 4 mL of toluene was performed under conditions similar to General Procedure for Epoxidation. GC; initial column temp, 70 °C; final column temp, 280 °C; progress rate, 7 °C min^{-1}; injection temp, 280 °C; split ratio, 100 : 1; t_R of (*Z*)-4-hexen-1-ol, 7.5 min; t_R of *cis*-3-methyloxiranepropanol, 8.3 min. Found: C, 61.95; H, 10.72%. Calcd for $C_6H_{12}O_2$: C, 62.04; H, 10.41%. ^{1}H NMR (400 MHz, $CDCl_3$) δ=1.16 (d, 3H, J=6.4 Hz), 1.51—1.59 (m, 1H), 1.83—1.99 (m, 3H), 2.53 (br, 1H), 3.57 (br, 1H), 3.63—3.70 (m, 1H), 3.77—3.86 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ=18.90, 26.27, 27.90, 68.07, 70.32, 83.74.

3,7-Dimethyl-2,3-epoxy-6-octen-1-ol.[38] A mixture of 131.9 mg (0.40 mmol) of $Na_2WO_4 \cdot 2H_2O$, 3.40 g (30 mmol) of aqueous 30% H_2O_2, 22.2 mg (0.20 mmol) of $NH_2CH_2PO_3H_2$, and 93.2 mg (0.20 mmol) of $[CH_3(n\text{-}C_8H_{17})_3N]HSO_4$ was vigorously stirred at room temperature for 15 min and then cooled to 0 °C. To this was added 3.09 g (20 mmol) of 3,7-dimethyl-2,6-octadien-1-ol;

the mixture was stirred at 0 °C for 2 h with stirring at 1000 rpm. The organic phase was separated, washed with 5 mL of saturated aqueous $Na_2S_2O_3$, and chromatographed on silica gel (BW 300, 150 g; eluent, 5 : 1 hexane–ether) to give 2.79 g (82%) of 3,7-dimethyl-2,3-epoxy-6-octen-1-ol as a colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ=1.30 (s, 3H), 1.44—1.51 (m, 1H), 1.61 (s, 3H), 1.68 (s, 3H), 2.05—2.13 (m, 2H), 2.39—2.46 (m, 1H), 3.00 (dd, 1H, J=4.4, 6.8 Hz), 3.62—3.73 (m, 1H), 3.78—3.89 (m, 1H), 5.04—5.12(m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ=16.67, 17.57, 23.60, 25.60, 38.42, 61.27, 61.38, 63.09, 123.24, 132.11.

Epoxidation of 3,7-Dimethyl-2,6-octadien-1-yl Pivalate. A round-bottomed flask was charged with 131.9 mg (0.40 mmol) of $Na_2WO_4 \cdot 2H_2O$, 22.2 mg (0.20 mmol) of $NH_2CH_2PO_3H_2$, 3.40 g (20 mmol) of aqueous 30% H_2O_2, and 93.2 mg (0.20 mmol) of $[CH_3(n\text{-}C_8H_{17})_3N]HSO_4$. After the mixture was vigorously stirred at room temperature for 20 min, 5.05 g (20 mmol) of 3,7-dimethyl-2,6-octadien-1-yl pivalate was added. This mixture was heated at 60 °C for 1 h with stirring at 1000 rpm. The organic phase was separated, washed with 5 mL of saturated aqueous $Na_2S_2O_3$, and chromatographed on silica gel (BW 300, 150 g; eluent, 5 : 1 hexane–ether) to give 1.98 g (37%) of 3,7-dimethyl-6,7-epoxy-2-octen-1-yl pivalate[39] and 2.57 g (48%) of 3,7-dimethyl-2,3 : 6,7-diepoxyoctyl pivalate as a colorless liquid.

3,7-Dimethyl-6,7-epoxy-2-octen-1-yl Pivalate: ^{1}H NMR (400 MHz, $CDCl_3$) δ=1.02 (s, 9H), 1.26 (s, 3H), 1.31 (s, 3H),1.63—1.69 (m, 2H), 1.73 (s, 3H), 2.11—2.27 (m, 2H), 2.19 (s, 3H), 2.70 (t, 1H, J=6.4 Hz), 4.58 (d, 2H, J=6.8 Hz), 5.36—5.43 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ=16.36, 18.64, 24.74, 27.01, 29.54, 36.06, 47.87, 58.24, 60.59, 63.76, 119.11, 140.92, 172.19.

3,7-Dimethyl-2,3 : 6,7-diepoxyoctyl Pivalate: Found: C, 66.75; H, 9.88%. Calcd for $C_{14}H_{26}O_4$: C, 66.64; H, 9.69%. ^{1}H NMR (400 MHz, $CDCl_3$) δ=1.04 (s, 9H), 1.27 (d, 3H, J=3.2 Hz), 1.31 (s, 3H), 1.33 (d, 3H, J=4.4 Hz), 1.61—1.71 (m, 4H), 2.70—2.74 (m, 1H), 3.02 (dd, 1H, J=4.8, 6.4 Hz), 4.05—4.10 (m, 1H), 4.27—4.33 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ=16.60, 18.58, 24.70, 29.53, 34.71, 35.11, 47.64, 59.30, 59.81, 62.61, 63.54, 63.70, 171.98.

Epoxidation of 2-Cyclohexen-1-yl Pivalate. A round-bottomed flask was charged with 131.9 mg (0.40 mmol) of $Na_2WO_4 \cdot 2H_2O$, 22.2 mg (0.20 mmol) of $NH_2CH_2PO_3H_2$, 3.40 g (20 mmol) of aqueous 30% H_2O_2, and 93.2 mg (0.20 mmol) of $[CH_3(n\text{-}C_8H_{17})_3N]HSO_4$. After the mixture was vigorously stirred at room temperature for 20 min, 3.93 g (20 mmol) of 2-cyclohexen-1-yl pivalate was added. This mixture was heated at 60 °C for 2 h with stirring at 1000 rpm. The organic phase was separated, washed with 5 mL of saturated aqueous $Na_2S_2O_3$, and chromatographed on silica gel (BW 300, 150 g; eluent, 10 : 1 hexane–ether) to give 0.24 g (6%) of *c*-2,*c*-epoxy-*r*-1-cycloehexyl pivalate and 2.81 g (66%) of *t*-2,*t*-3-epoxy-*r*-1-cyclohexyl pivalate as a colorless liquid.

***c*-2,*c*-3-Epoxy-*r*-1-cyclohexyl Pivalate:** Found: C, 66.33; H, 9.10%. Calcd for $C_{11}H_{18}O_3$: C, 66.64; H, 9.15%. ^{1}H NMR (400 MHz, $CDCl_3$) δ=1.05 (s, 9H), 1.28—1.37 (m, 1H), 1.52—1.63 (m, 3H), 1.83—1.86 (m, 2H), 3.30 (br, 2H), 5.12—5.16 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ=19.23, 22.55, 24.53, 29.53, 47.91, 52.77, 54.08, 70.24, 171.97.

***t*-2,*t*-3-Epoxy-*r*-1-cyclohexyl Pivalate:** Found: C, 66.65; H, 9.52%. Calcd for $C_{11}H_{18}O_3$: C, 66.64; H, 9.15%. ^{1}H NMR (400 MHz, $CDCl_3$) δ=1.05 (s, 9H), 1.28—1.37 (m, 2H), 1.43—1.50 (m, 1H), 1.78—1.89 (m, 2H), 1.98—2.03 (m, 1H), 3.06 (d, 1H, J=3.4 Hz), 3.23 (br, 1H), 5.07 (t, 1H, J=6.2 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ=14.50, 23.61, 25.82, 29.55, 47.94, 52.46, 53.34, 67.55, 171.25.

2-Phenyloxirane.[40] The reaction was run in a manner identical with the General Procedure for Epoxidation using styrene in 10 mL of toluene at a stirring rate of 250 rpm. GC; initial column temp, 70 °C; final column temp, 280 °C; progress rate, 9 °C min^{-1}; injection temp, 280 °C; split ratio, 100 : 1; t_R of styrene, 7.4 min; t_R of 2-phenyloxirane, 9.5 min. ^{1}H NMR (400 MHz, $CDCl_3$) δ=2.77 (dd, 1H, J=2.4, 5.2 Hz), 3.11 (dd, 1H, J=4.0, 5.2 Hz), 3.83 (dd, 1H, J=2.4, 4.0 Hz), 7.22—7.35 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$) δ=51.09, 52.24, 125.39, 128.08, 128.40, 137.52.

2-(*p*-*t*-Butylphenyl)oxirane. *p*-*t*-Butylstyrene in 10 mL of toluene was subjected to epoxidation at a stirring rate of 250 rpm. GC; initial column temp, 70 °C; final column temp, 280 °C; progress rate, 9 °C min^{-1}; injection temp, 280 °C; split ratio, 100 : 1; t_R of *p*-*t*-butylstyrene, 13.2 min; t_R of 2-(*p*-*t*-butylphenyl)oxirane, 15.4 min. Found: C, 81.41; H, 9.44%. Calcd for $C_{12}H_{16}O$: C, 81.77; H, 9.15%. ^{1}H NMR (400 MHz, $CDCl_3$) δ=1.31 (s, 9H), 2.80 (dd, 1H, J=2.4, 5.6 Hz), 3.11 (dd, 1H, J=4.0, 5.6 Hz), 3.83 (dd, 1H, J=2.4, 4.0 Hz), 7.19—7.23 (m, 2H), 7.34—7.39 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ=31.27, 34.54, 50.99, 52.20, 125.24, 125.40, 134.50, 151.25.

2-(*p*-Nonylphenyl)oxirane. The epoxide was obtained by epoxidation using a 10-mL flask, 33.0 mg (0.10 mmol) of $Na_2WO_4 \cdot 2H_2O$, 5.6 mg (0.05 mmol) of $NH_2CH_2PO_3H_2$, 850 mg (30 mmol) of aqueous 30% H_2O_2, 23.3 mg (0.05 mmol) of $[CH_3(n\text{-}C_8H_{17})_3N]HSO_4$, 1.15 g (5.0 mmol) of *p*-nonylstyrene, and 2.5 mL of toluene. GC (column, DB-1, 0.25 mm×60 m, GL Sciences Inc.); initial column temp, 120 °C; final column temp, 280 °C; progress rate, 10 °C min^{-1}; injection temp, 280 °C; split ratio, 100 : 1; t_R of *p*-nonylstyrene, 20.6 min; t_R of 2-(*p*-nonylphenyl)oxirane, 22.5 min. Found: C, 82.87; H, 10.89%. Calcd for $C_{17}H_{26}O$: C, 82.87; H, 10.64%. ^{1}H NMR (400 MHz, $CDCl_3$) δ=0.88 (t, 3H, J=6.0 Hz), 1.26—1.29 (m, 12H), 1.60 (br, 2H), 2.58 (t, 2H, J=8.0 Hz), 2.78 (dd, 1H, J=2.6, 5.6 Hz), 3.10 (dd, 1H, J=4.0, 5.6 Hz), 3.81 (dd, 1H, J=2.6, 4.0 Hz), 7.13—7.18 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ=14.04, 22.62, 29.27, 29.39, 29.45, 29.49, 31.42, 31.83, 35.61, 50.97, 52.26, 125.39, 128.47, 134.66, 143.00.

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