Aerobic Epoxidation of Olefinic Compounds Catalyzed by Tris(1,3-diketonato)iron(III)

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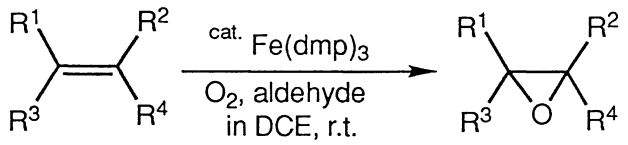
Tris[1,3-bis(*p*-methoxyphenyl)-1,3-propanedionato]iron(III) ($Fe(dmp)_3$) was found to be an excellent catalyst for oxygenation of a number of olefinic compounds including styrene analogues and olefinic alcohols into the corresponding epoxides in good to quantitative yields with combined use of molecular oxygen and an aldehyde at room temperature.

Iron complexes are considered to be one of the most promising catalysts for oxygenation, because iron is a relatively inexpensive and less poisonous metal compared with other transition metals.[1] Therefore much research works have been made for iron complex-catalyzed epoxidation of olefins with various oxidants, such as iron(III) porphyrins/iodosobenzene[2a] and sodium hypochlorite,[2b] or iron(III) perchlorate/α-siloxyalkyl perbenzoate.[2c] Molecular oxygen can also be used for epoxidation of olefins by employing the following catalysts; iron(III) porphyrins/O_2/H_2 on colloidal platinum,[2d] iron(III) complexes of artificial bleomycin/O_2/2-mercaptoethanol[2e] or (μ_3-oxo)triiron cluster $[Fe_3O(OCOR)_6L_3]$.[2f] In the above epoxidation reactions, however, the limitation of substrates, olefinic compounds, remained as an important problem to be solved.

Through our continued study on the aerobic epoxidation of olefins catalyzed by oxovanadium(IV) complexes[3a] or nickel(II) complexes,[3b–e] it could be pointed out that the behavior of the active oxidant generated from transition metal complexes with combined use of molecular oxygen and reductants is different from that of generally employed epoxidation reagents, such as *m*-chloroperbenzoic acid (*m*CPBA). For example, in the aerobic epoxidation of styrene (**1**) catalyzed by nickel(II) complex,[3f] styrene oxide (**2**) was obtained but in unsatisfactory yield (34%) accompanying C=C bond fission of styrene (**1**) into benzaldehyde (**3**, 31% yield), and similar results were also reported by other researchers.[2e,4] Recently, $Pr(OAc)_3$ was shown as an effective catalyst for the aerobic epoxidation of olefins in the coexistence of an aldehyde.[5] Taking the above results into account, our interests were focused on finding a suitable common transition metal catalyst which might be employed in the oxidation of a wide variety of olefinic compounds. After screening several metal complexes, it was found that tris(1,3-diketonato)-iron(III) has an excellent catalytic activity on aerobic epoxidation far better than bis(1,3-diketonato)iron(II). Of several tris(1,3-diketonato)iron(III) catalysts, tris-[1,3-bis(*p*-methoxyphenyl)-1,3-propanedionato]iron(III) ($Fe(dmp)_3$) (**11a**) was found to be the most effective catalyst for epoxidation of olefinic compounds with an atmospheric pressure of oxygen and an aldehyde at room temperature. Concerning the similar iron(III) complex, epoxidation of propylene with molecular oxygen and crotonaldehyde catalyzed by tris(acetylacetonato)iron(III) have already been reported to proceed in low conversion (<40%).[6]



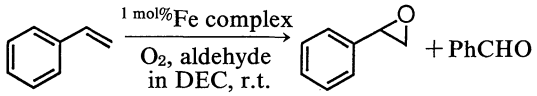
Scheme 1.

Results and Discussion

Epoxidation of Styrene Catalyzed by Various Iron Complexes. As mentioned before, styrene (**1**) is highly reactive toward oxygenation and rather difficult to obtain styrene oxide (**2**) selectively due to C=C bond cleavage of styrene (**1**) into benzaldehyde (**3**). Thus, in order to examine the effect of iron complexes for aerobic epoxidation, styrene (**1**) was taken as a model substrate and treated with combination of molecular oxygen and an aldehyde in 1,2-dichloroethane (DCE) at room temperature in the presence of a catalytic amount of bis- or tris(acetylacetonato)iron complexes (see Table 1). Of several iron(II) and iron(III) complexes, the highest yield of styrene oxide (**2**) was achieved when Fe(III)(acac)$_3$ (**6**) was employed as a catalyst (Entry 3).

Thus, various tris(1,3-diketonato)iron(III) type catalysts were prepared and their catalytic activities in aerobic epoxidation of styrene (**1**) were examined. As shown in Table 2, undesired cleavage of C=C bond was

Table 1. Epoxidation of Styrene (**1**) Catalyzed by Bis- or Tris(acetylacetonato)iron[a]



1 **2** **3**

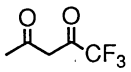
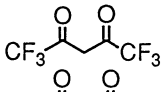
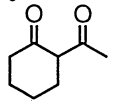
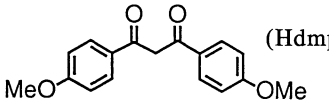
Entry	Iron complex	Time/h	Conversion/%[b]	Yield/%[b]	
				2	**3**
1	$Fe(II)(acac)_2$ (**4a**)	8	67	44	9
2	$Fe(III)(acac)_2Cl$ (**5**)	8	66	37	10
3	$Fe(III)(acac)_3$ (**6**)	10	100	82	8

a) Reaction conditions; styrene (**1**) 3.0 mmol, 2-ethylbutyraldehyde 18.0 mmol, iron complex 0.03 mmol (1.0 mol%) in 1,2-dichloroethane (DCE) 10.0 ml, O_2 1 atm. b) Determined by GC analysis.

suppressed when 1,3-diketones having electron-donating substituents, such as 2-acetylcyclohexanone (=Hach **9b**), 3-methyl-2,4-pentanedione (=Hmac **10b**) or 1,3-bis(*p*-methoxyphenyl)-1,3-propanedione (=Hdmp **11b**) were used, and the yield of styrene oxide (**2**) was improved up to 87—89% (Entries 4—6). Meanwhile, 1,3-diketones having electron-withdrawing substituents, such as 1,1,1-trifluoro-2,4-pentanedione (=Htfa **7a**) or 1,1,1,5,5,5-hexafluoro-2,4-pentanedione (=Hhfa **8b**), were not so efficient for selective epoxidation of styrene (**1**) (Entries 2 and 3).

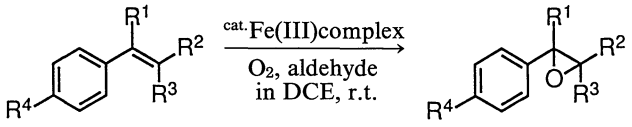
Several styrene analogues, such as *cis*-1-phenylpropene (**13**), *p*-chlorostyrene (**15**) or *trans*-stilbene (**17**), were also oxygenated in the above procedure by using iron(III) complexes (see Entries 2—4 in Table 3). In all cases, the corresponding epoxides, 1-phenyl-1,2-epoxy-

Table 2. Epoxidation of Styrene (**1**) Catalyzed by Various Iron(III) Complexes ($Fe(III)L_3$)[a]

Entry	Catalyst		Ligand(LH)		Time/h	Conversion/%[b]	Yield/%[b]	
							2	**3**
1	$Fe(III)(acac)_3$	(**6**)		(Hacac) (**4b**)	10	100	82	8
2	$Fe(III)(tfa)_3$	(**7a**)		(Htfa) (**7b**)	13	99	74	12
3	$Fe(III)(hfa)_3$	(**8a**)		(Hhfa) (**8b**)	13	100	59	22
4	$Fe(III)(ach)_3$	(**9a**)		(Hach) (**9b**)	13	100	87	8
5	$Fe(III)(mac)_3$	(**10a**)		(Hmac) (**10b**)	9	100	88	12
6	$Fe(III)(dmp)_3$	(**11a**)		(Hdmp) (**11b**)	9	100	89	10

a) Reaction conditions; styrene (**1**) 3.0 mmol, 2-ethylbutyraldehyde 18.0 mmol, iron(III) complex 0.03 mmol (1.0 mol%) in 1,2-dichloroethane (DCE) 10.0 ml, O_2 1 atm. b) Determined by GC analysis.

Table 3. Epoxidation of Styrene Analogues[a]



Entry	Styrene analogue					Time/h	Epoxide	Yield/%
	R^1	R^2	R^3	R^4				
1	H	H	H	H	(**1**)	9	Styrene oxide (**2**)	89[c]
2[b]	H	H	Me	H	(**13**)	14	1-Phenyl-1,2-epoxypropane (**14**)	Quant.[c,d]
3	H	H	H	Cl	(**15**)	14	2-(*p*-Chlorophenyl)oxirane (**16**)	Quant.[c]
4[b]	H	Ph	H	H	(**17**)	14	*trans*-Stilbene oxide (**18**)	99[e]

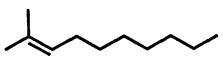
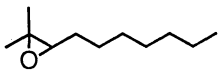
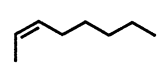
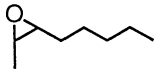
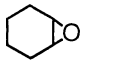
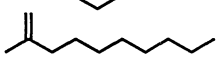
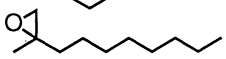
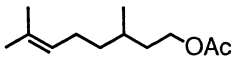
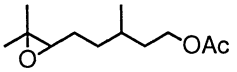
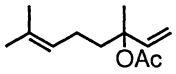
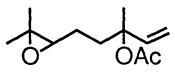
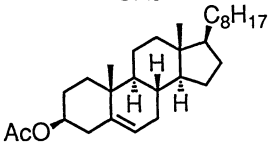
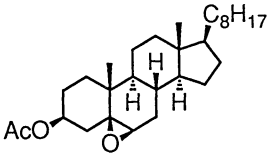
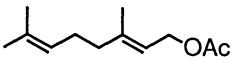
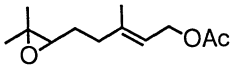
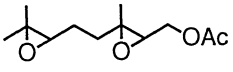
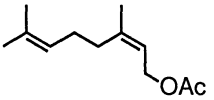
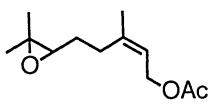
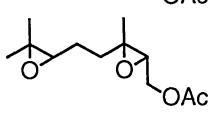
a) Reaction conditions; styrene analogues 3.0 mmol, 2-ethylbutyraldehyde 18.0 mmol, $Fe(dmp)_3$ (**11a**) 0.03 mmol (1.0 mol%) in 1,2-dichloroethane (DCE) 10.0 ml, O_2 1 atm, r.t. b) $Fe(acac)_3$ (**6**) 0.03 mmol was used. c) GC yield. d) Mixture of *cis* and *trans* isomers (11/89). e) Isolated yield.

propane (**14**), 2-(*p*-chlorophenyl)oxirane (**16**), or *trans*-stilbene oxide (**18**) were obtained in quantitative yields respectively without any undesirable over-oxidation as cleavage of C=C double bond affording aromatic aldehydes.

Epoxidation of Various Olefinic Compounds Catalyzed by Fe(dmp)$_3$ (11a). The above procedure was also successfully applied to various olefinic compounds. Aliphatic trisubstituted, 1,2-disubstituted or *exo*-terminal olefins afforded the corresponding epoxides in high to quantitative yields (see Entries 1—4 in Table 4). And in the case of cyclohexene (**23**), undesirable allylic oxidation affording 2-cyclohexen-1-ol was suppressed down to 5%. In a similar fashion, the corresponding epoxides were obtained in quantitative yields from acetates of olefinic alcohol, such as citronellyl acetate (**27**) and linalyl acetate (**29**) (Entries 5 and 6). Cholesteryl acetate (**31**) was selectively oxygenated into the corresponding β-epoxide **32** similar to the nickel(II)-catalyzed epoxidation.[3f] In the cases of geranyl acetate (**33**) and neryl acetate (**36**), double bonds at C^6–C^7 position were oxygenated preferentially over allylic double bonds, and the corresponding epoxides were obtained as mixtures of monoepoxides **34**, **37** and diepoxides **35**, **38** (Entries 8 and 9).

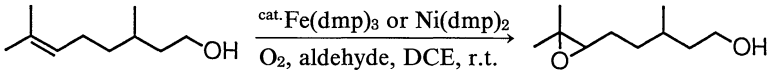
Epoxidation of Olefinic Alcohols Catalyzed by Fe(dmp)$_3$ (11a). Since olefinic alcohols were not efficiently oxygenated into the corresponding epoxy alcohols by using nickel(II) complexes, iron(III) complex-catalyzed epoxidation of citronellol (**39**), an olefinic alcohol, was examined. As shown in Table 5, epoxy alcohol **40** was obtained in quantitative yield without any over-oxidation of hydroxyl group by using Fe(dmp)$_3$ (**11a**) as a catalyst (Entry 1), whereas nickel(II) complex-catalyzed epoxidation of citronellol (**39**) stopped half-way and yield of epoxy alcohol **40** was moderate (Entry 2). It was assumed that nickel(II) complex was deactivated due to the undesirable coordination by hydroxyl group of olefinic alcohol, while iron(III) complexes having three 1,3-diketone ligands might not be preferable for

Table 4. Fe(dmp)$_3$ Catalyzed Epoxidation of Various Olefinic Compounds[a]

Entry	Olefin		Time/h	Epoxide		Yield/%
1		(**19**)	4		(**20**)	Quant.[b]
2		(**21**)	12		(**22**)	95[b,d]
3		(**23**)	12		(**24**)	80[b]
4		(**25**)	7		(**26**)	98[b]
5		(**27**)	7		(**28**)	Quant.[b]
6		(**29**)	12		(**30**)	Quant.[c]
7		(**31**)	12		(**32**)	86[c,e]
8		(**33**)	7		(**34**)	50[c]
					(**35**)	38[c]
9		(**36**)	12		(**37**)	69[c]
					(**38**)	28[c]

a) Reaction conditions; olefin 3.0 mmol, isobutyraldehyde 9.0 mmol, Fe(dmp)$_3$ (**11a**) 0.03 mmol (1.0 mol%), 1,2-dichloroethane (DCE) 10 ml, r.t., O_2 1 atm. b) Determined by GC analysis. c) Isolated yield. d) Mixture of *cis* and *trans* isomers (65/35). e) Mixture of α and β isomers (29/71).

Table 5. Epoxidation of Citronellol (**39**)[a]



39 **40**

Entry	Catalyst		Time/h	Conversion of **39**/%	Yield of **40**/%[b]
1	$Fe(dmp)_3$	(**11a**)	4.5	100	Quant.
2	$Ni(dmp)_2$	(**12a**)	4.5	67[b]	57

a) Reaction conditions; citronellol (**39**) 3.0 mmol, isobutyraldehyde 18.0 mmol, catalyst 0.03 mmol (1.0 mol%) in 1,2-dichloroethane (DCE) 10.0 ml, O_2 1 atm. b) Isolated.

Table 6. Epoxidation of Olefinic Alcohols[a]

Entry	Olefinic alcohol	Time/h	Epoxy alcohol	Yield/%
1	Citronellol (**39**)	4.5	3,7-Dimethyl-6,7-epoxyoctan-1-ol (**40**)	Quant.[b]
2	3-Methyl-3-buten-1-ol (**41**)	14	3-Methyl-3,4-epoxybutan-1-ol (**42**)	Quant.[c]
3	*cis*-3-Hexen-1-ol (**43**)	14	3,4-Epoxyhexan-1-ol (**44**)	80[c,d]
4	*trans*-2-Hexen-1-ol (**45**)	14	*trans*-2,3-Epoxyhexan-1-ol (**46**)	67[c]

a) Reaction conditions; olefinic alcohol 3.0 mmol, isobutyraldehyde 18.0 mmol, $Fe(dmp)_3$ (**11a**) 0.03 mmol (1.0 mol%) in 1,2-dichloroethane (DCE) 10.0 ml, O_2 1 atm. b) Isolated yield. c) GC yield. d) Mixture of *cis* and *trans* isomers (1/1).

the coordination by hydroxyl function.

Further, several olefinic alcohols, such as homoallylic alcohol **41** and **43**, or allylic alcohol **45** were oxygenated into the corresponding epoxy alcohols in good to quantitative yields (see Entries 2—4 in Table 6).

Conclusion

A wide variety of epoxides were prepared by the aerobic epoxidation of olefinic compounds including styrene analogues or olefinic alcohols in good to quantitative yields by using tris(1,3-diketonato)iron(III) complex, and particularly tris[1,3-bis(*p*-methoxyphenyl-1,3-propanedionato]iron(III) ($Fe(dmp)_3$) (**11a**) was found to be the most excellent catalyst in present oxygenation.

Experimental

General: Melting points were measured on a Mettler FP62 apparatus and uncorrected.

(a) Spectrometers: IR spectra were obtained by using a JASCO Model IR-700 infrared spectrometer on KBr pellets or liquid film on KBr. ^1H NMR spectra were recorded with a JEOL Model FX-270 spectrometer using $CDCl_3$ as solvent and with tetramethylsilane as internal standard.

(b) Chromatography: GC-analysis were performed on a Shimadzu GC-15A using a glass capillary column (Shimadzu CBP-l0, 25 m), and the peak areas were obtained with a Shimadzu chromatopack CR-5A.

Preparation of 1,3-Diketones and Tris(1,3-diketonato)iron-(III) Complexes. Tris(acetylacetonato)iron(III) (**6**, $Fe(acac)_3$) were purchased from Tokyo Kasei Kogyo Co., Ltd. (TCI) Bis(acetylacetonato)iron(II) (**4a**, $Fe(acac)_2$),[7] chlorobis(acetylacetonato)iron(III) (**5**, $Fe(acac)_2Cl$),[8] tris(1,1,1-trifluoro-2,4-pentanedionato)iron(III) (**7a**, $Fe(tfa)_3$),[9] tris(1,1,1,5,5,5-hexafluoro-2,4-pentanedionato)iron(III) (**8a**, $Fe(hfa)_3$),[10] tris-(2-acetylcyclohexanonato)iron(III) (**9a**, $Fe(ach)_3$),[11] and tris(3-methyl-2,4-pentanedionato)iron(III) (**10a**, $Fe(mac)_3$)[12] were prepared according to the reported methods, respectively, and ligands were purchased from TCI Co., Ltd. (**4b, 7b, 8b,** and **9b**) and Aldrich Chemical Company, Inc. (**10b**), respectively.

1,3-Bis(*p*-methoxyphenyl)-1,3-propanedione (11a, Hdmp);[3c,13] A refluxing suspension of sodium hydride (0.39 mol) in cyclohexane (400 ml), a solution of *p*-methoxyacetophenone (0.33 mol) and ethyl *p*-methoxybenzoate (0.33 mol) in cyclohexane (200 ml) was added over 1 h, and reflux was continued for another 2 h. After cooling, reaction mixture was quenched with 1.0 mol dm^{-3} aqueous HCl, then crude product was extracted with THF–Et_2O. The organic extract was washed with brine, and dried over anhydrous sodium sulfate, then solvent was removed in vacuo. Recrystallization from hexane–ethyl acetate gave slightly colored needles (58% yield): Mp 131—138 °C; ^1H NMR ($CDCl_3$) δ=3.90 (6H, s), 6.80 (1H, s), 7.00 (4H, m), 7.95 (4H, m); IR (KBr) 2938, 2840, 1687, 1605, 1507, 1429, 1305, 1263, 1230, 1170 cm^{-1}

Tris[1,3-bis(*p*-methoxyphenyl)-1,3-propanedionato]iron-(III) (11b, Fe(dmp)$_3$); To a stirred mixture of Hdmp (30.0 mmol) in THF–MeOH (1/1, 100 ml), an aqueous solution of $FeCl_3$ (10.0 mmol, 50 ml) was added over 10 min. Precipitated reddish-brown solid was filtered and washed with MeOH and water. After drying in vacuo (90 °C/0.1 mmHg, 1 mmHg=133.322 Pa), $Fe(dmp)_3$ **11a** was yielded as reddish-purple solid. Found: C, 66.78; H, 5.18%. Calcd for $C_{45}H_{45}O_{12}Fe$: C, 64.83; H, 5.44%.

Melting Points and IR Spectra of Iron Complexes. Bis-(acetylacetonato)iron(II) (4a, Fe(acac)$_2$); Red solid; mp 169.0—169.4 °C; IR (KBr) 2918, 1571, 1562, 1525, 1376, 1270 cm^{-1}.

Chlorobis(acetylacetonato)iron(III) (5, Fe(acac)$_2$Cl); Red solid; mp 180.4—181.0 °C; IR (KBr) 2992, 2918, 1571, 1525, 1364, 1290 cm^{-1}.

Tris(1,1,1-trifluoro-2,4-pentanedionato)iron(III) (7a, Fe(tfa)$_3$); Orange solid; mp 212.4—212.8 °C; IR (KBr) 1615, 1510, 1292, 1147 cm^{-1}.

Tris(1,1,1,5,5-hexafluoro-2,4-pentanedionato)iron(III) (8a,

Fe(hfa)$_3$); Yellowish-orange solid; mp 162.0—162.6 °C; IR (KBr) 1647, 1619, 1565, 1540, 1445, 1255, 1210, 1146 cm^{-1}.

Tris(2-acetylcyclohexanonato)iron(III) (9a, Fe(ach)$_3$); Reddish-purple solid; mp 228.6—229.0 °C; IR (KBr) 2930, 2854, 1573, 1460, 1374, 1331, 1278 cm^{-1}.

Tris(3-methyl-2,4-pentanedionato)iron(III) (10a, Fe(mac)$_3$); Reddish-purple solid; mp 189.6—190.0 °C; IR (KBr) 2998, 2960, 2918, 1876, 1574, 1467, 1424, 1360, 1330, 1292 cm^{-1}.

Tris[1,3-bis(*p*-methoxyphenyl)-1,3-propanedionato]iron-(III) (11a, Fe(dmp)$_3$) Reddish-purple solid; mp 278.0—279.4 °C; IR (KBr) 2930, 2836, 1604, 1587, 1527, 1492, 1377, 1305, 1257, 1228, 1175 cm^{-1}.

Epoxidation of 1,5-Dimethyl-1-vinyl-4-hexenyl Acetate (Linalyl Acetate, 31). (see Entry 6 in Table 5). A mixture of linalyl acetate (**29**) (3.0 mmol), Fe(III)(dmp)$_3$ (**11a**) (0.03 mmol, 1.0 molo%), isobutyraldehyde (9.0 mmol) in 1,2-dichloroethane (10.0 ml) was stirred under an atmospheric pressure of oxygen at room temperature for 12 h. Reaction mixture was washed with saturated aqueous $NaHCO_3$ solution, and, after drying over anhydrous sodium sulfate, solvent was removed in vacuo. Purification of the residue by column chromatography on SiO_2 (hexane–ethyl acetate) afforded 1-(3,4-epoxy-4-methylpentyl)-1-methylallyl acetate (**30**) (639 mg, quantitative yield).

^{1}H NMR and IR Spectra of Epoxides (in Tables 3—6). Styrene Oxide (2), 1,2-Epoxycyclohexane (24). ^{1}H NMR spectra, IR spectra and retention time in GC analysis agreed with those of the authentic samples.

***cis*-1-Phenyl-1,2-epoxypropane (14);** ^{1}H NMR ($CDCl_3$) δ=1.09 (3H, d, J=5.28 Hz), 3.34 (1H, dq, J_1=5.28 Hz, J_2=4.29 Hz), 4.06 (1H, d, J=4.29 Hz), 7.3 (5H, m); IR (neat) 3028, 2996, 2994, 2928, 1496, 1451, 1259 cm^{-1}.

2-(*p*-Chlorophenyl)oxirane (16); ^{1}H NMR ($CDCl_3$) δ=2.75 (1H, m), 3.14 (1H, m), 3.83 (1H, m), 7.21 (2H, d, J=8.57 Hz) 7.32 (2H, d, J=8.57 Hz); IR (neat) 3050, 2990, 2918, 1495, 1089 cm^{-1}.

***trans*-Stilbene Oxide (18);** ^{1}H NMR ($CDCl_3$) δ=3.86 (2H, s), 7.3—7.4 (10H, m); IR (KBr) 3060, 3030, 2974, 1606, 1497, 1452 cm^{-1}.

2,3-Epoxy-2-methyldecane (20); ^{1}H NMR ($CDCl_3$) δ=0.88 (3H, t, J=6.92 Hz), 1.26 (3H, s,), 1.28 (10H, m), 1.31 (3H, s), 1.50 (2H, m), 2.71 (1H t, J=6.27 Hz); IR (neat) 2925, 2850, 1465 cm^{-1}.

***cis*-2,3-Epoxyoctane (22);** ^{1}H NMR ($CDCl_3$) δ=0.93 (3H, t, J=7.09 Hz), 1.27 (3H, d, J=5.28 Hz), 1.35—1.45 (4H, m), 1.48—1.55 (4H, m), 2.90 (1H, m), 3.06 (1H, m); IR (neat) 2958, 2928, 2856, 1466, 1381 cm^{-1}.

1,2-Epoxy-2-methyldecane (26); ^{1}H NMR ($CDCl_3$) δ=0.88 (3H, t, J= 6.80 Hz), 1.27 (3H, s), 1.29 (14H, m), 2.55 (1H, d, J=10.9 Hz), 2.57 (1H, d, J=10.9 Hz); IR (neat) 2924, 2852, 1465 cm^{-1}.

6,7-Epoxy-3,7-dimethyloctyl Acetate (28); ^{1}H NMR ($CDCl_3$) δ=0.94 (3H, d, J=6.27 Hz), 1.27 (3H, s), 1.31 (3H, s) , 1.40—1.60 (7H, m), 2.05 (3H, s) , 2.70 (1H, t, J=6.06 Hz), 4.11 (2H, m); IR (neat) 2960, 2924, 2872, 1741, 1461, 1379, 1367, 1241 cm^{-1}.

1-(3,4-Epoxy-4-methylpentyl)-1-methylallyl Acetate (30); ^{1}H NMR ($CDCl_3$) δ=1.20 (3H, d, J=6.92 Hz), 1.26 (3H, s), 1.30 (3H, s), 1.5—1.6 (4H, m), 2.00 (3H, s), 2.71 (1H, t, J=6.26 Hz), 5.15 (2H, m), 5.95 (1H, m); IR (neat) 2974, 2932, 1738, 1461, 1372, 1249 cm^{-1}.

5,6-Epoxycholesteryl Acetate (32) Mixture of α and β Isomers; ^{1}H NMR ($CDCl_3$) δ=0.60 (3H, m), 0.80—1.60 (6H, m), 1.80—2.20 (34H, m), 2.00 (3H, s), 2.90 (0.29H, d, J=2.90 Hz, H-6β), 3.10 (0.71H, d, J=2.00 Hz, H-6α), 4.70—5.00 (1H, m) IR (KBr) 2950, 1734, 1470, 1368, 1247, 1041 cm^{-1}.

***trans*-6,7-Epoxy-3,7-dimethyl-2-octenyl Acetate (34);** ^{1}H NMR ($CDCl_3$) δ=1.26 (3H, s), 1.31 (3H, s), 1.60—1.80 (5H, m), 2.05 (3H, s), 2.10—2.30 (2H, m), 2.70 (1H, t, J=6.26 Hz), 4.59 (2H, d, J=7.25 Hz), 5.40 (1H, m); IR (neat) 2960, 2926, 1740, 1454, 1380, 1234 cm^{-1}.

***cis*-2,3 : 6,7-Diepoxy-3,7-dimethyloctyl Acetate (35);** ^{1}H NMR ($CDCl_3$) δ=1.30 (6H, m), 1.50—1.80 (7H, m), 2.10 (3H, s), 2.70 (1H, m), 3.05 (1H, m), 4.05 (1H, m), 4.30 (1H, m); IR (neat) 2970, 2929, 1743, 1455, 1380, 1232 cm^{-1}.

***cis*-6,7-Epoxy-3,7-dimethyl-2-octenyl Acetate (37);** ^{1}H NMR ($CDCl_3$) δ=1.27 (3H, s), 1.31 (3H, s), 1.63 (2H, dt, J_1=7.75 Hz, J_2=6.27 Hz), 1.78 (3H, s), 2.05 (3H, s), 2.26 (2H, t, J=7.75 Hz), 2.71 (1H, t, J=6.27 Hz), 4.58 (2H, d, J=6.60 Hz), 5.41 (1H, t, J=6.60 Hz); IR (neat) 2964, 2930, 1739, 1670, 1453, 1379, 1234 cm^{-1}.

***trans*-2,3 : 6,7-Diepoxy-3,7-dimethyloctyl Acetate (38);** ^{1}H NMR ($CDCl_3$) δ=1.28 (3H, s), 1.32 (3H, s), 1.35 (3H, s), 1.60—1.80 (4H, m), 2.10 (3H, s), 2.72 (1H, m), 3.00 (1H, m), 4.09 (1H, m), 4.35 (1H, m); IR (neat) 2970, 2931, 1744, 1455, 1378, 1234 cm^{-1}.

3,7-Dimethyl-6,7-epoxyoctan-1-ol (40); ^{1}H NMR ($CDCl_3$) δ=0.93 (3H, d, J=6.26Hz), 1.27 (3H, s), 1.30 (3H, s), 1.4—1.5 (2H, m), 1.5—1.8 (5H, m), 1.90 (1H, s), 2.7 (1H, t, J=6.10 Hz), 3.7 (2H, m); IR (neat) 3420, 2960, 2932, 2872, 1463 cm^{-1}.

3-Methyl-3,4-epoxybutan-1-ol (42); ^{1}H NMR ($CDCl_3$) δ= 1.39 (3H, s), 1.80—2.00 (2H, m), 2.66 (1H, d, J=4.29 Hz), 2.83 (1H, d, J=4.29 Hz), 3.70—3.80 (2H, m), 4.70 (1H, s); IR (neat) 3450, 2980, 1420 cm^{-1}.

***cis*-3,4-Epoxyhexan-1-ol (44);** ^{1}H NMR ($CDCl_3$) δ=1.05 (3H, t, J=7.59 Hz), 1.50—1.60 (2H, m), 1.65—1.75 (1H, m), 1.85—2.00 (1H, m), 2.94 (1H, dt, J_1=6.43 Hz, J_2=4.20 Hz), 3.23 (1H, dt, J_1=7.91 Hz, J_2=4.20 Hz), 3.65 (1H, s), 3.80—3.90 (9H, m); IR (neat) 3424, 2970, 2934, 2878, 1468, 1057 cm^{-1}.

***trans*-2,3-Epoxyhexan-1-ol (46);** ^{1}H NMR ($CDCl_3$) δ= 0.96 (3H, t, J=7.26 Hz), 1.40—1.60 (4H, m), 2.29 (1H, s), 2.95 (2H, m), 3.61 (1H, m), 3.92 (1H, m); IR (neat) 3412, 2960, 2932, 2872, 1464 cm^{-1}.

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