An effective procedure for the synthesis of acid-sensitive epoxides: Use of 1-methylimidazole as the additive on methyltrioxorhenium-catalyzed epoxidation of alkenes with hydrogen peroxide†

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An effective method for suppression of ring opening and rearrangement of acid-sensitive epoxides during methyltrioxorhenium(MTO)-catalyzed epoxidation of alkenes with H_2O_2 by using 1-methylimidazole as a co-additive has been found. The combined use of 3-methylpyrazole and 1-methylimidazole as the additives has been found to be an effective procedure that affords excellent yields of acid-sensitive epoxides for MTO-catalyzed epoxidation.

Introduction

Methyltrioxorhenium(VII) (CH_3ReO_3, MTO) as an oxidation catalyst was first reported by Herrmann and co-workers in 1991 for the epoxidation of alkenes with hydrogen peroxide (H_2O_2) as the terminal oxidant.[1] Since then, MTO-catalyzed H_2O_2 oxidations have been explored with a variety of substrates,[2] such as alkanes,[3] alkynes,[4] arenes,[5] phenols,[6] cyclic ketones (Baeyer–Villiger oxidation),[7] benzaldehydes,[8] organonitrogen compounds,[9] organosulfur compounds,[10] alcohols,[11] and so on.[12] The important features of MTO as a catalyst are its availability (ease of synthesis,[13] now commercially available[14]), its stability in air (dioxygen and humidity), and its solubility in various solvents, including water.[15] Furthermore, H_2O_2 is an environmentally advantageous oxidizing agent, since its only waste by-product is water.[16]

Epoxidation is an important transformation of alkenes, because epoxides are versatile intermediates in organic synthesis.[17] The use of transition metal complexes as the epoxidation catalyst is of particular interest, due to their ability to activate environmentally benign oxidants such as molecular oxygen[18] and H_2O_2.[16,17,19] MTO has emerged as one of the most active catalysts for alkene epoxidation in the presence of H_2O_2 as the terminal oxidant.[20–29]

At a first stage, MTO-catalyzed epoxidation was investigated in a homogeneous medium using *t*-BuOH as solvent with anhydrous H_2O_2.[1] While high yields of certain epoxides may be obtained by this procedure, the main disadvantage, however, was the low selectivity in the cases of acid-sensitive epoxides were formed. The Lewis acidity of the rhenium center caused hydrolysis and concomitant cleavage of the epoxide ring leading to the formation of 1,2-diols in the presence of water.[1]

Several methods have been investigated to overcome this problem. Herrmann and co-workers have reported that addition of Lewis base-ligand suppresses the epoxide ring-opening by reducing the Lewis acidity of the rhenium center.[1] However, while the selectivity toward epoxides increases, the activity of the catalytic system decreases.

A major improvement in the MTO-catalyzed epoxidation was achieved by Sharpless and co-workers.[20a] They reported that biphasic system and addition of a significant excess of pyridine relative to the catalyst not only suppresses the ring-opening but also accelerates the alkene epoxidation.

Shortly afterward further improvements were reported by the groups of Sharpless and Herrmann. It was found that the use of 3-cyanopyridine[20b] and pyrazole[22b] as the Lewis base additives is more effective and less problematic than the use of pyridine, since pyridine is easily oxidized to pyridine N-oxide that is a less efficient additive.[22a] Recently we reported 3-methylpyrazole as a superior additive to pyridines and pyrazole because MTO/3-methylpyrazole system has higher catalytic activity and longer catalyst lifetime than MTO/pyridines and MTO/pyrazole systems.[29]

However, even under these improved conditions, the hydrolysis or rearrangement of particular acid-sensitive epoxides proceeds and produces a significant amount of diols or rearrangement products.[26c–d,28a–b] Therefore, there still is a strong need for further improvement of MTO-catalyzed epoxidation to produce acid-sensitive epoxides in high yield.

Herein we wish to report an improved method of MTO-catalyzed epoxidation of alkenes to produce acid-sensitive epoxides in high yields. During our research on the effect of additives for the MTO-catalyzed epoxidation,[29] we found 1-methylimidazole to be an excellent additive that strongly suppresses the ring opening and rearrangement of acid-sensitive epoxides. The combined use of 3-methylpyrazole and 1-methylimidazole afforded acid-sensitive epoxides in excellent yields within reasonable reaction times.

Results and discussion

Indene epoxidation

We first examined MTO-catalyzed epoxidation of indene **1**. Indene oxide **2** is known to be very prone to ring-opening by acid-catalyzed hydrolysis, and it is difficult to obtain high yield of indene oxide by catalytic epoxidations including MTO-catalyzed epoxidation.[20a,28a–b,30] In order to evaluate the effect of

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various additives for indene epoxidation, we compared pyridine,[20a] pyrazole,[22b] 3-methylpyrazole,[29] and 1- methylimidazole in MTO-catalyzed epoxidation of indene **1**.

The time courses of indene **1** consumption and epoxide **2** formation by 0.2 mol% MTO-catalyzed epoxidation are indicated in Fig. 1. Although indene **1** was consumed rapidly by the oxidation without additive, only a small amount of indene oxide **2** was detected. The main product is corresponding diol **3** with minor amount of oxidatively C–C bond cleaved product **4**[31] (Scheme 1). The epoxidation of indene **1** with pyrazole or 3-methylpyrazole as the additive proceeded smoothly and produce indene oxide **2** over 70% yield within 1 h. However, the epoxide decomposed under the reaction conditions to diol **3** and oxidatively C–C cleaved product **4**, and the amount of indene oxide **2** decreased rapidly by time course. The epoxidation of indene **1** with pyridine additive stopped within 1 h at 62% conversion, probably because pyridine was rapidly oxidized to pyridine oxide under the reaction conditions.[9f,22a] Interestingly, the epoxide **2** was not affected under the reaction conditions. On the other hand, the epoxidation of indene **1** with 1-methylimidazole as the additive indicated different results. The initial rate of epoxidation of indene **1** with 1-methylimidazole was slower than that of the reaction without any additives. However, indene **1** was consumed steadily, and indene oxide **2** was produced correspondingly and survived under the reaction conditions. These results indicate that the addition of 1-methylimidazole retards the rate of the epoxidation, while the ring opening reaction of epoxide was strongly suppressed.

From the above results, we have expected to obtain a high yield of indene oxide **2** within a reasonable reaction time by the combined use of 3-methylpyrazole and 1-methylimidazole as the additives for MTO-catalyzed epoxidation. Fig. 2 showed the time profile of conversion of indene **1** and the yield of indene oxide **2** in the cases of single use of 10 mol% 3-methylpyrazole and combined use of 10 mol% 3-methylpyrazole and 1 mol% 1-methylimidazole.

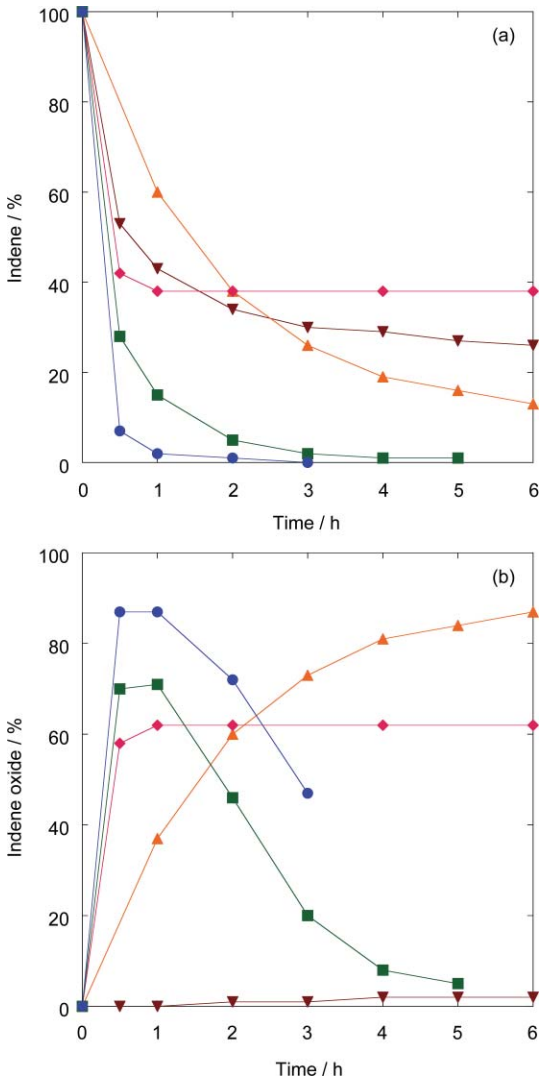


Fig. 1 Time course of MTO-catalyzed epoxidation of indene **1** with various additives. (a) Consumption of indene **1**. (b) Production of indene oxide **2**. Conditions: indene **1** (10 mmol), 35% H_2O_2 (20 mmol), MTO (0.02 mmol), additive (1.0 mmol), in CH_2Cl_2 (5 mL) at rt. Analysis by GC. (●) Curve A: 3-Methylpyrazole. (■) Curve B: Pyrazole. (♦) Curve C: Pyridine. (▲) Curve D: 1-Methylimidazole. (▼) Curve E: No additive.

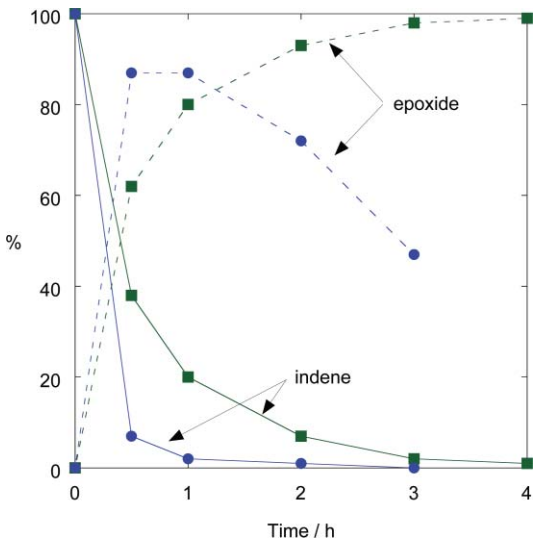
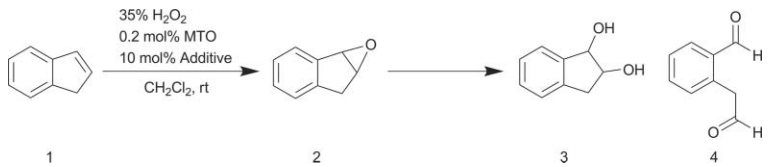


Fig. 2 Time course of MTO-catalyzed epoxidation of indene **1** in the presence of (●) 10 mol% 3-methylpyrazole and (■) 10 mol% 3-methylpyrazol + 1 mol% 1-methylimidazole. Conditions: indene **1** (10 mmol), 35% H_2O_2 (20 mmol), MTO (0.02 mmol), and additive(s) in CH_2Cl_2 (5 mL) at rt. Analysis by GC.



Scheme 1 MTO catalyzed epoxidation of indene.

As expected, indene oxide **2** was obtained quantitatively within 4 h by combined use of 3-methylpyrazole and 1-methylimidazole.

The necessary amount of 1-methylimidazole as the additive for the combined use with 3-methylpyrazole was examined. As shown in Fig. 3, the amount of 1-methylimidazole added could be reduced to 0.2 mol% (equal amount to MTO) without large reduction of the epoxide yield.

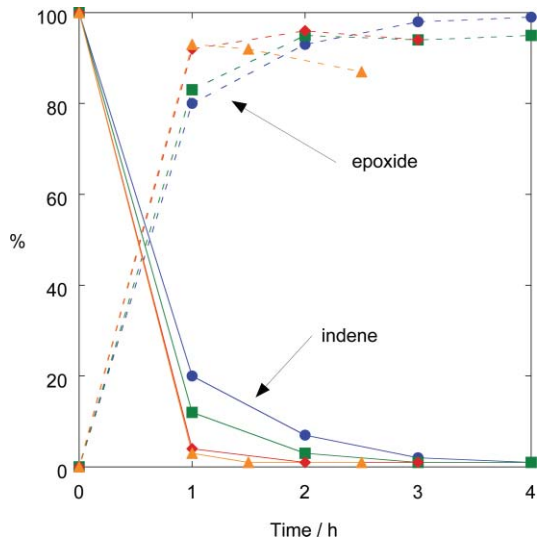


Fig. 3 Time course of MTO-catalyzed epoxidation of indene **1** in the presence of 10 mol% 3-methylpyrazole and varying amount of 1-methylimidazole. Conditions: indene **1** (10 mmol), 35% H_2O_2 (20 mmol), MTO (0.02 mmol), 3-methylpyrazole (1 mmol) and 1-methylimidazole (0.1–0.01 mmol) in CH_2Cl_2 (5 mL) at rt. Analysis by GC. (●) Curve A: 1 mol% (0.1 mmol) 1-methylimidazole. (■) Curve B: 0.5 mol% (0.05 mmol) 1-methylimidazole. (◆) Curve C: 0.2 mol% (0.02 mmol) 1-methylimidazole. (▲) Curve D: 0.1 mol% (0.01 mmol) 1-methylimidazole.

Various imidazoles were examined as the additive for MTO-catalyzed epoxidation (Fig. 4). Imidazole, 4-methylimidazole, 1,2-dimethylimidazole and 2-methylimidazole were inferior additives than 1-methylimidazole. 1-Butylimidazole showed comparable effect with 1-methylimidazole.

The role of 1-methylimidazole is to protect indene oxide from acid-catalyzed ring-opening reaction. Heterocycles having higher basicity coordinate stronger to rhenium metal of MTO, thereby decreasing the Lewis acidity of the rhenium more effectively.[20d] 1-Methylimidazole (pK_a 7.3)[32] has higher basicity than pyrazole (pK_a 2.5), 3-methylpyrazole (pK_a 3.6), and pyridine (pK_a 5.2). Furthermore, 1-methylimidazole does not undergo N-oxidation by MTO/H_2O_2 oxidation system.

The basicity of substituted imidazoles examined in Fig. 4 is not so different to 1-methylimidazole (pK_a of imidazole 7.0, 1-butylimidazole 7.1, 4-methylimidazole 7.6, 2-methylimidazole 7.9, 1,2-dimethylimidazole 8.0).[32,33] The reason why only the imidazoles substituted by alkyl group at 1-position are effective additives for MTO-catalyzed epoxidation is not clear at this stage, and further study on the substituent effect of imidazole is in progress.

The MTO-catalyzed epoxidation of styrenes that produce acid-sensitive epoxides in the presence of both 3-methylpyrazole and 1-methylimidazole was examined. The results are summarized in Table 1. Substituted styrenes such as isosafrole **5** and

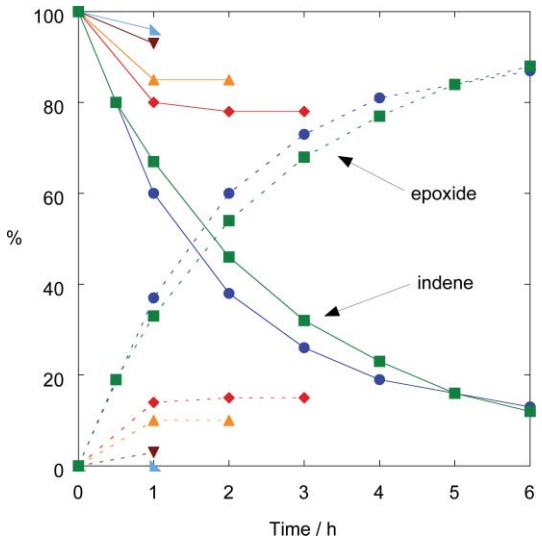


Fig. 4 Time course of MTO-catalyzed epoxidation of indene **1** in the presence of various imidazoles. Conditions: indene **1** (10 mmol), 35% H_2O_2 (20 mmol), MTO (0.02 mmol), and additive (1 mmol) in CH_2Cl_2 (5 mL) at rt. Analysis by GC. (●) Curve A: 1-methylimidazole. (■) Curve B: 1-butylimidazole. (◆) Curve C: imidazole. (▲) Curve D: 4-methylimidazole. (▼) Curve E: 1,2-dimethylimidazole. (▶) Curve F: 2-methylimidazole.

α-methylstyrene **6**, afforded corresponding epoxides quantitatively (Entries 3 and 5). Although the epoxidation of isosafrole **5** and α-methylstyrene **6** in the presence of 3-methylpyrazole as the sole additive afforded corresponding epoxides in high yields at first, prolonged reaction caused the decomposition of the epoxides formed (Entries 4 and 6).

2,2-Dimethyl-2*H*-chromene epoxidation

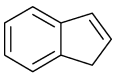
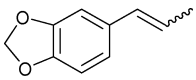
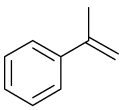
Chromenes (2*H*-1-benzopyran derivatives) and 3,4-epoxychroman derivatives have attracted much attention because of their biological activity and their importance as synthetic intermediates for biologically active compounds.[34–36] The conventional epoxidation using *m*-chloroperbenzoic acid (*m*CPBA) was not suitable for the preparation of 3,4-epoxychromans. The epoxidation of 2,2-dimethyl-2*H*-chromene **7** by *m*CPBA under buffered conditions was reported to give the corresponding epoxide **8** only 46% yield along with 33% ketone **9** (Scheme 2).[34a,b]

MTO-catalyzed epoxidation of 2,2-dimethyl-2*H*-chromene **7** with 3-methylpyrazole as the additive resulted in 93% epoxide **8** along with 4% diol **10** by 2 h reaction at 97% conversion (Table 2, Entry 1). The ketone **9** was not observed under the reaction conditions. Prolonged reaction time did not increase the yield of epoxide **8** and the yield of diol **10** increased (Entry 2). The epoxidation of the chromene **7** with 10 mol% 3-methylpyrazole and 1 mol% 1-methylimidazole afforded 99% epoxide **8** with trace amount (<1%) of diol **10** (Entry 3).

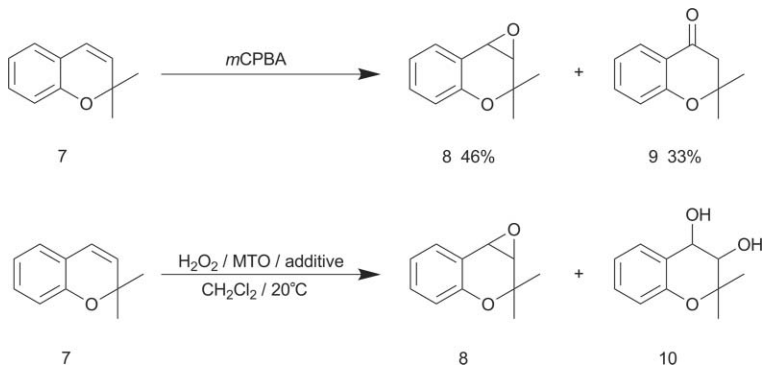
Epoxidation of bishomoallylic alcohols

The epoxidation of bishomoallylic alcohols often resulted in the formation of cyclic ethers (furan and pyran compounds). This is because the epoxides initially formed are unstable under the

Table 1 MTO-catalyzed epoxidation of indene and styrenes in the presence of 3-methylpyrazole and 1-methylimidazole[a]

Entry	Alkene	Additive	MTO (mol%)	Time/h	Conversion (%)[b]	Epoxide (%)[b]
1		A	0.2	4	>99	99
2		B	0.2	1[c]	98	87 (89)
				2[d]	>99	72
	1					
3		A	0.1	3	>99	99
4		B	0.1	1[c]	97	79 (81)
				2[d]	>99	59
	5					
5		A	0.2	5	>99	>99
6		B	0.2	1[c]	97	96 (99)
				2[d]	>99	87
	6					

[a] General conditions: alkene (10 mmol), 35% H_2O_2 (20 mmol), MTO, and additive(s) in CH_2Cl_2 (5 mL) at rt. Additive A: 3-methylpyrazole (1.0 mmol) and 1-methylimidazole (0.1 mmol). Additive B: 3-methylpyrazole (1.0 mmol). [b] Determined by GC analysis. Yields based on alkenes used. The numbers in parentheses are the yields based on alkenes consumed. [c] Time at maximum epoxide yield. [d] Time at conversion of alkene over 99%.



Scheme 2 Epoxidation of 2,2-dimethyl-2*H*-chromene

Table 2 MTO-catalyzed epoxidation of 2,2-dimethyl-2*H*-chromene **7**[a]

Entry	Additive (mol%)	Time/h	Conversion (%)[b]	Epoxide **8** (%)[b,c]	Diol **10** (%)[b,c]
1	3MePz (10)	2	97	93	4
2	3MePz (10)	3	>99	90	9
3	3MePz (10) + 1MeIm (1)	7	>99	99	<1

[a] General conditions: 2,2-dimethyl-2*H*-chromene **7** (10 mmol), 35% H_2O_2 (20 mmol), MTO (0.02 mmol), and additive(s) in CH_2Cl_2 (5 mL) at 20 °C. Additive: 3-methylpyrazole (3MePz), 1-methylimidazole (1MeIm). [b] Determined by GC analysis. [c] Yields based on alkene used.

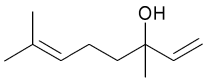
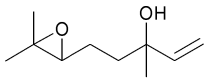
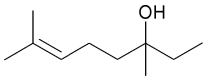
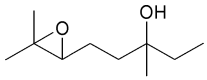
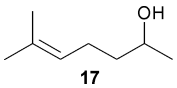
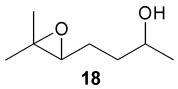
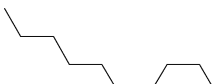
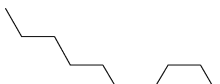
reaction conditions (generally acidic) and easily rearrange to a mixture of furans and pyrans by an intramolecular reaction. The mainly obtained products by epoxidation of bishomoallylic alcohols with peracids and most of catalytic epoxidation systems are such cyclic ethers.[37,38,40a,c,e]

MTO-catalyzed epoxidation of bishomoallylic alcohols has been reported to produce epoxides and/or cyclic ethers according to the reaction conditions. Sharpless and co-workers reported that a bishomoallylic alcohol (4-penten-1-ol) gave only furan in high yield in the presence of 3-cyanopyridine as the additive.[20b] Espenson's group reported the formation of furans exclusively by MTO-catalyzed oxidation of bishomoallylic alcohols without any amine additives.[23h] Rudler and co-workers reported that they observed the formation of epoxide **12** by MTO-catalyzed epoxidation of linalool **11** with bipyridine as the additive but they obtained the epoxide **12** only 10% yield.[26d] On the other hand, Jacobs and co-workers reported that the use of large amount of pyridine additives (combined use of pyridine and 3-cyanopyridine, 40 mol% each) afforded the 6,7-epoxide of linalool **12** in good yield (82%) with small amount of the cyclic ethers **13** (6%) and **14**.[26c]

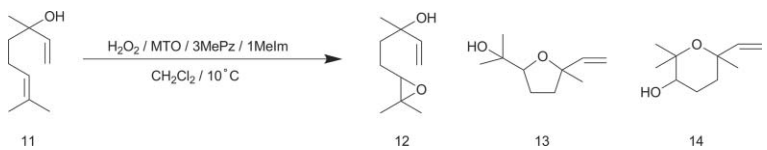
The combined use of 10 mol% 3-methylpyrazole and 1 mol% 1-methylimidazole as the additives on MTO-catalyzed epoxidation of linalool **11** afforded the corresponding epoxide **12** in 95% yield with very small amount (<2% total) of the cyclic ethers **13** and **14** (Scheme 3).

This procedure was successfully applied to various bishomoallylic alcohols. As shown in Table 3, acid-sensitive epoxides were obtained in excellent yields. Only a trace amount of cyclized products *via* acid-catalyzed intramolecular cyclization of initially produced epoxides were detected. These epoxidation could be performed also under organic solvent-free conditions[29b] without significant reduction of the epoxide yields (Entries 2, 4, and 6). In every bishomoallylic alcohol examined, a considerable amount

Table 3 MTO-catalyzed epoxidation of bishomoallylic alcohols in the presence of 3-methylpyrazole and 1-methylimidazole[a]

Entry	Alkene	Solvent	T/°C	Time/h	Epoxide	Yield (%)[b]
1	 **11**	CH_2Cl_2	10	2	 **12**	95
2		—[c]	10	1		94
3	 **15**	CH_2Cl_2	15	2	 **16**	99
4		—[c]	10	2		95
5	 **17**	CH_2Cl_2	15	2	 **18**	99
6		—[c]	10	1		97
7[d]	 **19**	CH_2Cl_2	20	4	 **20**	99[e]

[a] Conditions: alkene (10 mmol), 35% H_2O_2 (12 mmol), MTO (0.01 mmol), 3-methylpyrazole (1.0 mmol), 1-methylimidazole (0.1 mmol), CH_2Cl_2 (5 mL) or without organic solvent. [b] Analysis by GC. [c] Reaction without organic solvent. [d] Reaction with 0.02 mmol MTO. [e] Isolated yield of crude epoxide. See experimental and ESI for detail.†



11 12 13 14

Scheme 3 MTO-catalyzed epoxidation of linalool

of cyclization products were produced without the addition of 1-methylimidazole.

Epoxidation of terpenes

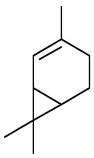
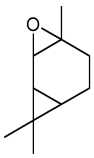
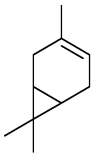
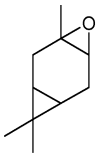
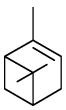
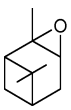
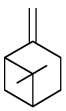
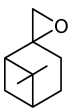
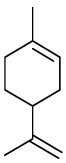
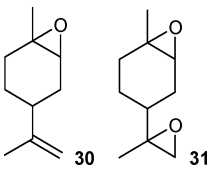
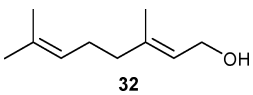
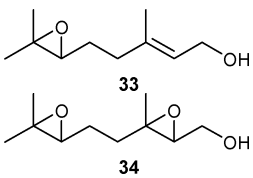
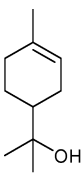
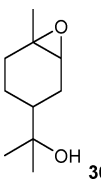
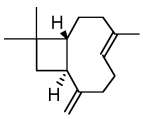
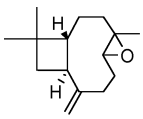
Terpenes are widely available from nature, and their epoxides are important starting materials for the synthesis of fragrances, flavors, therapeutically active substances, and pharmaceuticals.[39] Organic peroxides, particularly peracetic acid and *m*CPBA, are still the most widely used for the epoxidation of terpenes. Although a number of metal-catalyzed epoxidations with H_2O_2 as oxidant have been reported,[40] the epoxidation of terpenes is still a challenging task due to the sensitivity of epoxy terpenes under acidic conditions.[41] Terpenes and their epoxides easily undergo ring opening, rearrangement, double-bond migration, and hydrolysis by acid catalysis or by heating. Though some MTO-catalyzed epoxidation of terpenes have been reported,[25b–d,26a,c,d] the results reported are not fully satisfactory, because of the use of CH_2Cl_2 as solvent and/or the complicated multistep preparation of immobilized catalysts.

The application of above mentioned MTO-catalyzed epoxidation with combined use of 3-methylpyrazole and 1-methylimidazole as the additives successfully afforded terpene epoxides in excellent yields. Some examples are summarized in Table 4. 2-Carene **21** and 3-carene **23** provided excellent yield of corresponding epoxides **22** and **24** both under organic solvent-free conditions and in CH_2Cl_2 (Entries 1, 3, 5, and 6). The epoxidation 2-carene **21** without 1-methylimidazole resulted in lower yield of the epoxide **22**, that decomposed during prolonged reaction (Entry 2). This procedure can easily be carried out on a 10 g scale of 3-carene epoxidation (Entry 6). α-Pinene **25** and β-pinene **27** also provided excellent yield of corresponding epoxides **26** and **28** (Entries 7–10). Although Saladino and co-workers reported excellent results of catalytic epoxidation of (+)-3-carene **23** and α-pinene **25** by using microencapsulated Lewis base adduct of MTO, low reaction temperature (–10 °C) and use of CH_3CN–CH_2Cl_2 as the reaction solvent were required.[25b–d]

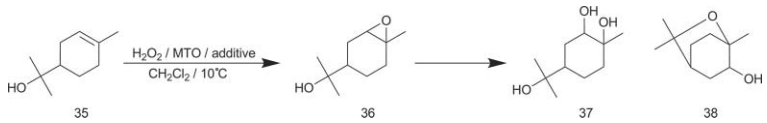
Limonene **29** afforded 1,2-epoxide **30** as the main product along with diepoxide **31** (Entry 12). The use of excess H_2O_2 and prolonged reaction time resulted in the selective formation of diepoxide **31** (Entry 13). Geraniol **32** afforded the mixture of 6,7-epoxide **33** and diepoxide **34** under organic solvent-free conditions (Entry 14). The epoxides **30**, **31**, **33**, and **34** were stable enough under the reaction conditions without 1-methylimidazole.

MTO-catalyzed epoxidations of α-terpineol **35** with 3-methylpyrazole as the sole additive afforded 94% yield of epoxide **36** within 1 h (Entry 17). After leaving the reaction mixture at room temperature for 20 h, the epoxide **36** decreased to 37% and triol **37** and rearrangement product 2-hydroxy-1,8-cineol **38** increased (Scheme 4). The epoxidation of α-terpineol **35** with combined use of 10 mol% 3-methylpyrazole and 1 mol% 1-methylimidazole afforded 97% epoxide **36** (Entry 16). After 20 h,

Table 4 MTO-catalyzed epoxidation of terpenes[a]

Entry	Alkene	MTO (mol%)	Additive[b]	Solvent	Time/h	Conv (%)[c]	Epoxide	Yield (%)[c]
1	 **21**	0.2	A	—[d]	3	>99	 **22**	>99
2		0.2	B	—[d]	1	75		63 (84)
					2	94		66 (70)
					3	98		35 (36)
3	 **23**	0.1	A	CH_2Cl_2	2	>99	 **24**	>99
4		0.1	B	CH_2Cl_2	2	>99		99
5		0.3[e]	A	—[d]	6	>99		>99
6		0.2	A	CH_2Cl_2	2.5	>99		>99
								94[f]
7	 **25**	0.3[e]	A	—[d]	5	>99	 **26**	95
8		0.2	A	CH_2Cl_2	4	>99		91
9	 **27**	0.2	A	—[d]	6	>99	 **28**	82
10		0.2	A	CH_2Cl_2	2.5	>99		94
11		0.2	B	CH_2Cl_2	1.5	>99		92
12[g]	 **29**	0.2	B	—[d]	3	97	 **30** **31**	83[h], 14[i]
13[g,j]		0.2	B	CH_2Cl_2	8	100		1[h], 98[i]
14[g]	 **32**	0.2	B	—[d]	0.5	93	 **33** **34**	74[j], 14[i] (80[k], 15[i])
15	 **35**	0.05	A	—[d]	2	>99	 **36**	97
16		0.1	A	CH_2Cl_2	1.5	>99		97[l]
17		0.1	B	CH_2Cl_2	1	>99		94[m]
18	 **39**	0.1[n]	A	CH_2Cl_2	1	>99	 **40**	>99

[a] General conditions: alkene (10 mmol), 35% H_2O_2 (20 mmol or 12 mmol), at 10 °C. [b] Additives A: 3-methylpyrazole (1.0 mmol) and 1-methylimidazole (0.1 mmol). Additives B: 3-methylpyrazole (1.0 mmol). [c] Analysis by GC. Yields based on alkenes used. The numbers in parentheses are the yields based on alkenes consumed. [d] Reaction without organic solvent. [e] Addition of 0.2 mol% MTO at start, and additional MTO (0.1 mol%) at 1 h. [f] Isolated yield after distillation. [g] Reaction at 15 °C. [h] 1,2-Epoxide. [i] Diepoxide. [j] 25 mmol H_2O_2 was used. [k] 6,7-Epoxide. [l] 90% of epoxide remaining in the reaction mixture after leaving for 20 h at rt. [m] 37% of epoxide remaining in the reaction mixture after leaving for 20 h at rt. [n] Addition of 0.06 mol% MTO at start, and additional MTO (0.04 mol%) at 30 min.



Scheme 4 MTO-catalyzed epoxidation of α-terpineol

90% of the epoxide **36** has survived in the reaction mixture. These results also clearly indicate the effect of 1-methylimidazole for the suppression of epoxide decomposition. This epoxidation also proceeded smoothly under organic solvent-free conditions with 0.05 mol% MTO (Entry 15). Epoxidation of β-caryophyllene **39** was successfully produced the corresponding monoepoxide **40** (Entry 18).

Conclusions

We have found that addition of 1-methylimidazole strongly inhibits hydrolysis and rearrangement of acid-sensitive epoxides produced by MTO-catalyzed epoxidation, and that the combined use of 3-methylpyrazole and 1-methylimidazole could produce variety of acid-sensitive epoxides in excellent yields within reasonable reaction times. We demonstrated the efficiency of the procedure by producing variety of acid-sensitive epoxides from styrenes, a chromene, bishomoallylic alcohols, and terpenes in excellent yields.

Experimental

General remarks

All reagents obtained were from commercial sources unless otherwise noted and were used without further purification. Methyltrioxorhenium was prepared according to the reported procedure.[13b] 2,2-Dimethyl-2*H*-chromene was prepared according to the reported procedure.[42] The concentration of H_2O_2 was determined by iodometric titration before use. The progress of the reaction was monitored by GC analysis. The conversion of alkenes and yield of epoxides were determined by GC internal standard technique. GC analyses were performed on Shimadzu GC-2010 (FID detector) equipped with GL Sciences InertCap 1 column (30 m length x 0.25 mm ID x 0.25 μm film thickness). GC-MS analyses (EI) were performed on ThermoQuest GCQplus with Trace2000GC equipped with GL Sciences InertCap 1MS column (30 m length x 0.25 mm ID x 0.25 μm film thickness). ^{1}H (90 MHz) and ^{13}C NMR (22 MHz) were recorded on JEOL EX-90 spectrometer using $CDCl_3$ as solvent. The oxidation products were identified by comparison of physical data with commercial samples (1,2-dihydroxyindane **3** and linalool oxide (furano) **13** from TCI, linalool oxide (pyrano) **14** from Wako Pure Chemical) or reported data. Indene oxide **2**[30a,b,31,40b] 2-(2-oxoethyl)benzaldehyde **4**,[31] α-methylstyrene oxide,[43] 3,4-epoxy-2,2-dimethylchroman **8**,[34a] 6,7-epoxy-3,7-dimethyl-1-octen-3-ol **12**,[26d,34a] 6,7-epoxy-3,7-dimethyl-3-octanol **16**,[34a] 5,6-epoxy-6-methyl-2-heptanol **18**,[34a] 2-carene oxide **22**,[44] 3-carene oxide **24**,[25b–d,40b,f,41a,b,44] α-pinene oxide **26**,[25b,c,26d,40b,f,41b,44] β-pinene oxide **28**,[45] 1,2-epoxylimonene **30**,[25b–d,40f,44] bis-epoxylimonene **31**,[25d,44] 6,7-epoxygeraniol **33**,[25b,d] 2,3,6,7-bis-epoxygeraniol **34**,[25b,d] α-terpineol epoxide **36**,[40f] 2-hydroxy-1,8-cineole **38**,[46] β-caryophyllene oxide **40**[40f,41a] are reported previously. 3,4-Dihydroxy-2,2-dimethylchroman **10** and *p*-menthane-1,2,8-triol **37** were identified by GC-MS analysis (without isolation of the products).

Typical procedures for epoxidations

Indene (1) epoxidation (Table 1, Entry 1). A 50-mL flask equipped with a stirrer bar was charged with CH_2Cl_2, indene **1** (1.16 mL, 10 mmol), 3-methylpyrazole (81 μL, 1.0 mmol, 10 mol%), 1-methylimidazole (8 μL, 0.1 mmol, 1 mol%), and MTO (5 mg, 0.020 mmol, 0.2 mol%). H_2O_2 (35%, 1.68 mL, 20 mmol) was added all at once to the stirring solution. The resulted two-phase mixture was stirred vigorously (1000 rpm) at room temperature. The progress of the reaction was monitored at appropriate interval by GC analysis of small aliquots of the organic phase. The conversion of indene and yield of indene oxide were determined by GC internal standard method. The GC internal standard material (n-undecane) was added just before the first analysis.

NMR data of isosafrole oxide (Table 1. Entries 3 and 4, mixture of isomers). Ratio of *trans*:*cis* is approximately 4 : 1 by ^{1}H NMR. ^{1}H NMR (90 MHz, $CDCl_3$) δ_H 1.10 (d, J = 5.4 Hz, 3H, *cis*), 1.41 (d, J = 5.4 Hz, 3H, *trans*), 2.98 (dq, J = 5.4, 1.8 Hz, 1H, *trans*), 3.28 (dq, J = 5.4, 4.3 Hz, 1H, *cis*), 3.50 (d, J = 1.8 Hz, 1H, *trans*), 3.98 (d, J = 4.3 Hz, 1H, *cis*), 5.94 (s, 2H, *cis* and *trans*), 6.6–6.9 (m, 3H, *cis* and *trans*); ^{13}C NMR (22 MHz, $CDCl_3$) δ_C 12.4 (*cis*), 17.7 (*trans*), 55.1 (*cis*), 57.4 (*cis*), 58.7 (*trans*), 59.5 (*trans*), 101.0 (*cis* and *trans*), 105.6 (*trans*), 107.1 (*cis*), 108.0 (*cis*), 108.1 (*trans*), 119.5 (*trans*), 119.9 (*cis*), 131.7 (*trans*), 147.5 (*trans*), 148.0 (*trans*). The signals of quaternary carbons of *cis* isomer were not observed on the spectrum.

***cis*-4-Decen-1-ol (19) epoxidation (Table 3, Entry 7).** A 50 mL flask equipped with a stirrer bar was charged with CH_2Cl_2, *cis*-4-decen-1-ol **19** (1.83 mL, 10 mmol), 3-methylpyrazole (81 μL, 1.0 mmol, 10 mol%), 1-methylimidazole (8 μL, 0.1 mmol, 1 mol%) and MTO (5 mg, 0.020 mmol, 0.2 mol%). The mixture was cooled to 20 °C by immersing in a temperature controlled water bath. H_2O_2 (35%, 1.01 mL, 12 mmol) was added all at once to the stirring solution. The resulted two-phase mixture was stirred vigorously (1000 rpm) at 20 °C. The reaction was completed after 4 h. (The progress of the reaction was monitored by GC analysis.) The reaction mixture was poured into brine, and extracted with CH_2Cl_2. The organic layer was washed with aqueous $Na_2S_2O_3$, and then dried over anhydrous Na_2SO_4. The solvent of the organic layer was removed out by evaporator, and the residue was dried under vacuum. 1-Hydroxy-4,5-epoxydecane **20** (1.71 g, 99%) was obtained as pale yellow oil. An attempt of purification by vacuum distillation was failed by decomposition of the epoxide. 1-Hydroxy-4,5-epoxydecane **20**: ^{1}H NMR (90 MHz, $CDCl_3$) δ_H 0.7–1.9 (m, 16H), 2.4 (br s, 1H), 2.9 (m, 2H), 2.7 (t, J = 6 Hz, 2H); ^{13}C NMR (22 MHz, $CDCl_3$) δ_C 13.9, 22.4, 24.3, 26.1, 27.7. 29.7, 31.6, 57.0, 57.5, 62.2.

Procedure for 10g scale epoxidation of 3-carene (Table 4, Entry 6). A 200-mL flask equipped with a stirbar was charged with CH_2Cl_2 (35 mL), 3-carene (10 g, 73.4 mmol, 94% purity by GC), 3-methylpyrazole (0.59 mL, 7.3 mmol, 10 mol%), 1-methylimidazole (59 μL, 0.73 mmol, 1 mol%), and MTO (36.6 mg, 0.147 mmol, 0.2 mol%). The flask was cooled to 10 °C by applying an external cooling bath. H_2O_2 (35%, 7.4 mL, 88 mmol) was added dropwise to the stirring solution from dropping funnel (*ca.* 10 min). During the H_2O_2 addition the temperature of the solution was kept below 17 °C. The resulted two-phase mixture was stirred vigorously at 10 °C. The reaction was completed after 4 h, and the reaction mixture was poured into brine. The organic layer of reaction mixture was washed successively with brine (2 times) and with aqueous solution of $Na_2S_2O_3$. The organic layer was dried over anhydrous Na_2SO_4, and CH_2Cl_2 was distilled out by evaporator. Distillation of the residual oil under reduced pressure (9 Torr, 76–77 °C) afforded 3-carene oxide as colorless oil (10.5 g, 94% yield, 94% purity by GC). The physical data agreed with that previously reported.[25b–d,40b,f,41a,b,44]

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