Selective Oxidation of Monoterpenes with Hydrogen Peroxide Catalyzed by Peroxotungstophosphate (PCWP)

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Catalytic epoxidation of monoterpenes with aqueous hydrogen peroxide catalyzed by peroxotungstophosphate (PCWP) under biphase conditions using chloroform as the solvent was examined. A variety of terpenes was oxidized to the corresponding monoepoxides or diepoxides in good yields under mild conditions. For example, limonene (**1**) was converted into limonene oxide (**1a**) in which the cyclohexene double bond was selectively epoxidized in almost quantitative yield. The oxidation of γ-terpinene (**2**) with 2.2 equiv of 35% H_2O_2 took place with high stereoselectivity to give *cis*-diepoxide **2c**. In terpenes bearing electron-withdrawing groups such as neryl acetate (**3**), geranyl acetate (**4**), citral (**5**), and geranyl nitrile (**6**), the double bonds remote from the substituents were epoxidized in preference to the others. The epoxidation of linalool (**9**) by the present catalyst−oxidant system produced the cyclic products, hydroxy furan **9a** and hydroxy pyran **9b**, rather than epoxide. *tert*-Butyl alcohol was successfully employed as the solvent by treating a hydrogen peroxide solution of *tert*-butyl alcohol with $MgSO_4$ prior to use. The regioselectivities in the epoxidation of monoterpenes can be favorably explained from the electron densities of the double bonds which were estimated using the CAChe system.

Introduction

In the fine chemicals industry, the development of clean oxidation processes, in which toxic salts such as chromium and manganese salts are not utilized, has become very important in the interest of “no-waste” technologies. Molecular oxygen and hydrogen peroxide which ultimately do not generate salts are thus oxidants of great interest. Recent advances in the phase-transfer oxidation method using hydrogen peroxide, by which a wide variety of organic substrates can be oxidized have occurred as a result. Although many catalysts have been developed for this purpose, heteropolyoxometalates have received particular attention as homogeneous liquid-phase oxidation catalysts.[1] We have shown that the peroxotungstophosphate ($[C_5H_5N^+(CH_2)_{15}CH_3]_3\{PO_4[W(O)(O_2)_2]_4\}^{3-}$) (PCWP), which has both phase-transfer and good oxidizing capabilities catalyzes the oxidation of a wide variety of organic substrates using aqueous hydrogen peroxide as an oxidant.[2] The oxidation of alkenes with 35% H_2O_2 in the presence of PCWP in a two-phase system gives the corresponding epoxides in good yields.[2i] The application of the same methodology to alkynes and allenes, which are difficult to selectively oxidize by conventional oxidation methods, led to their first successful conversion into α,β-unsaturated ketones[2b] and/or α,β-epoxy ketones,[2g] and α-alkoxy ketones and/or α-hydroxy ketones,[2b] respectively. We have now examined the oxidation of monoterpenes by the PCWP−H_2O_2 system.

In general, the selective oxidation of monoterpenes is hard to achieve with peracids due to their oxidizing strength, by which mono- and diepoxides as well as cleaved products are simultaneously produced. For the epoxidation of acid-sensitive substrates, the reaction must be carried out in a buffered aqueous medium.[3] Recently, a few reagents such as dioxiranes[4] and $HOF{\cdot}CH_3CN$[5] have been developed for the selective epoxidation of monoterpenes. And catalytic oxidation systems consisting of Mo, V, or Mn complexes and alkyl hydroperoxides,[6] iodosylbenzene,[7] or sodium monoxychloride[8] have been also reported. However, there has been little study so far of terpene oxidation with hydrogen peroxide as the oxidant.

In this paper, we wish to report the selective oxidation of monoterpenes **1**−**9** to the corresponding mono- or diepoxides with aqueous hydrogen peroxide under the

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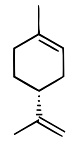
influence of a catalytic amount of heteropolyoxometalates. The regioselectivity of the present oxidation is discussed by considering the frontier electron density of each double bond in the terpenes.



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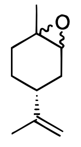

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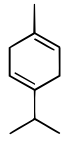

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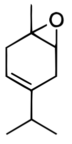

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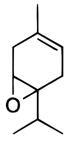

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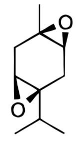

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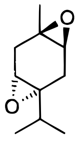

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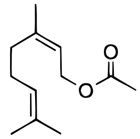

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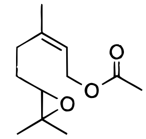

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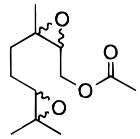

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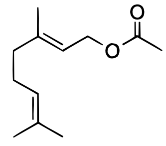

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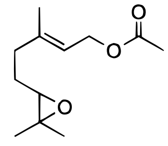

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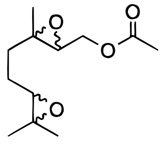

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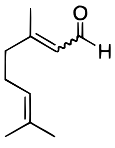

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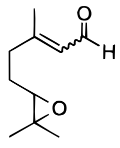

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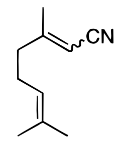

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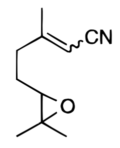

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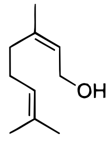

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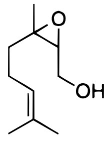

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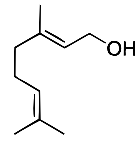

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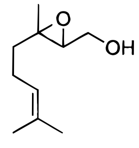

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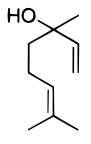

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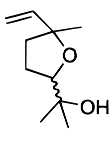

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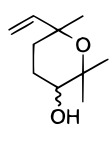

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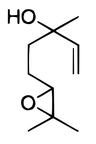

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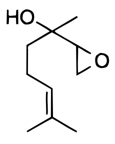

9d

Results

Limonene (**1**) was chosen as a model substrate and allowed to react with hydrogen peroxide by PCWP under various reaction conditions. The oxidation of **1** with 1.1 equiv of 35% H_2O_2 in the presence of a catalytic amount of PCWP (0.5 mol % with respect to **1**) in chloroform at room temperature proceeded regioselectively, but not stereoselectively, to afford a nearly 1:1 mixture of *cis*- and *trans*-limonene oxides (**1a**) in almost quantitative yield (Table 1, run 1). Even when the PCWP was reduced to 0.05 mol% from 0.5 mol% under these conditions, **1a** was obtained in high yield and the turnover number of the catalyst reached 1180 (run 2), although Hill *et al.* have stated that heteropolyoxometalates such as PCWP react with the resulting epoxide to generate an inactive inorganic species; hence the catalysis of the PCWP stops after a modest number of turnovers, up to 500, in the epoxidation of 1-octene.[9] Recently, Neumann has reported that a new type of polyoxometalate, $[WZnMn_2(ZnW_9O_{34})_2]^{12-}$, consisting of multiple components, shows higher catalytic turnovers, 2300, than the PCWP for the epoxidation of cyclooctene with 35% H_2O_2 under phase-transfer conditions.[10]

On the basis of these results, several monoterpenes were oxidized by the PCWP–H_2O_2 system (Table 1).

Table 1. Epoxidation of Various Monoterpenes with 35% H_2O_2 Catalyzed by PCWP[a]

run	substrate	H_2O_2 (equiv)	time (h)	conv (%)	products	selectivity (%)
1	**1**	1.1	1.5	94	**1a**	97
2[b]	**1**	1.1	24	89	**1a**	89
3	**2**	1.1	4	91	**2a**+**2b**	87[c]
					2c	12
4	**2**	1.1 + 1.1[d]	2	100	**2a** + **2b**	7
					2c[e]	79
5	**3**	0.6 + 0.6[a]	5	96	**3a**	56
					3b[f]	33
6	**3**	2.5	2	100	**3a**	20
					3b[f]	58
7	**4**	0.6 + 0.6[d]	5	100	**4a**	86
					4b[f]	11
8	**5**	1.1	6	84	**5a**	85
9	**6**	1.1	3	100	**6a**	99
10	**7**	0.6 + 0.6[d]	1	85	**7a**	65
11	**8**	0.6 + 0.6[d]	1	83	**8a**	61
12[g]	**8**	1.5	24	91	**8a**	98
13	**9**	1.1	1	100	**9a**[f]	48
					9b[f]	22

[a] Substrate (4 mmol) was allowed to react with 35% H_2O_2 in the presence of PCWP (0.02 mol, 0.5 mol %) at room temperature in $CHCl_3$ (5 mL). [b] 0.05 mol % of PCWP was used. [c] **2a**:**2b** = 90:10. [d] After stirring for 0.5 h, additional 35% H_2O_2 was used. [e] *cis*-**2c**:*trans*-**2c** = 95:5. [f] **3b**, **4b**, **9a**, and **9b** consisted of about 1:1 stereoisomeric mixture. [g] **8** (4 mmol) was allowed to react with 35% H_2O_2 in the presence of CMP (0.016 mol, 0.4 mol %) and $MgSO_4$ (0.08 g) at room temperature in $CHCl_3$ (10 mL).

γ-Terpinene (**2**) was epoxidized with 1.1 equiv of 35% H_2O_2 in 91% conversion to form a 9:1 regioisomeric mixture of monoepoxides **2a** and **2b** (87%) together with a small amout of the diepoxide, 1,2,4,5-diepoxy-*p*-menthane (**2c**) (12%) (run 3). When an additional 35% H_2O_2 (1.1 equiv) was added to this oxidation system after 30 min, **2c** was formed in preference to **2a** and **2b** (run 4). It is noteworthy that the present epoxidation of **2** produced *cis*-**2c** with high stereoselectivity (*cis*-**2c**/*trans*-**2c** = 95/5), because the epoxidation of **2** by *m*CPBA produces *trans*-**2c** rather than *cis*-**2c** (*cis*-**2c**/*trans*-**2c** = 30/70).[11] The regioselectivity in the epoxidation of **2** will be discussed later. The oxidation of neryl acetate (**3**) gave 6,7-epoxide **3a** along with diepoxide **3b** (run 5). By the use of 2.5 equiv of the oxidant with respect to **3**, **3b** was obtained as a major product (run 6). Geranyl acetate (**4**) was also oxidized to monoxide **4a** in good yield (run 7). It is interesting to note that the oxidation of citral (**5**) under these reaction conditions gave 3,7-dimethyl-6,7-epoxy-2-octen-1-al (**5a**) with good selectivity without transformation of the aldehyde function to a carboxylic

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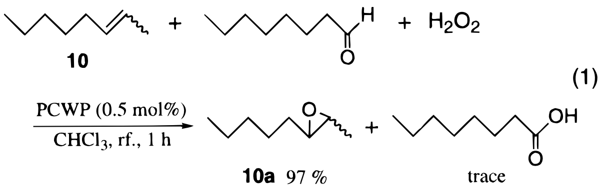
acid (run 8). These results show that the PCWP preferentially promotes the epoxidation of the double bonds over the oxidation of aldehydes to carboxylic acids. In fact, the oxidation of an equimolar mixture of 2-octene (**10**) and octanal by the PCWP−H_2O_2 system produced 2,3-epoxyoctane (**10a**) rather than octanoic acid (eq 1).



10

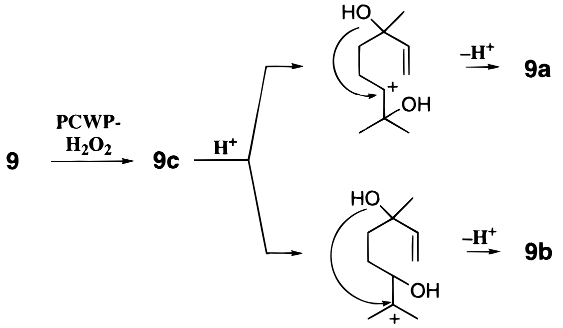
10a 97 %

trace

In the oxidation of geranyl nitrile (**6**), monoepoxide **6a**, in which the carbon−carbon double bond remote from a cyano group was selectively oxidized, was obtained with complete regioselectivity (run 9).

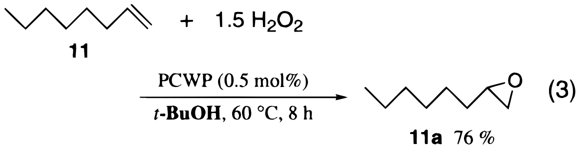
The oxidation of allylic monoterpenes such as nerol (**7**) and geraniol (**8**) afforded 2,3-epoxides, **7a** and **8a** as main products, in which allylic double bonds were preferentially oxidized (runs 10 and 11). The moderate selectivities in these epoxidations are believed to be due to the decomposition of the resulting epoxides by further oxidation by the PCWP−H_2O_2 system. Molybdenum heteropolyoxometalate, $[C_5H_5N^+(CH_2)_{15}CH_3]_3(PMo_{12}O_{40})^{3-}$ (CMP), which shows high selectivity for the epoxidation of allylic alcohols,[2j] was found to be suitable for the selective epoxidation of the allylic bonds of **7** and **8**. Thus, **8** was converted into **8a** with 35% H_2O_2 in the presence of a catalytic amount of CMP with 98% selectivity (run 12). On the other hand, linalool (**9**) was transformed to tetrahydrofuran derivative **9a** (48%) and tetrahydropyran derivative **9b** (22%) by the PCWP−H_2O_2 system (run 13). **9a** and **9b** are considered to be formed *via* an intramolecular cyclization of 3,7-dimethyl-6,7-epoxy-1-octen-3-ol (**9c**) resulting from the epoxidation of **9** as shown in Scheme 1. In contrast to the oxidation of **7** and **8** where the allylic double bonds were preferentially epoxidized, the inner double bond of **9** was more easily oxidized than the allylic one. A detailed consideration of the regioselectivity in the oxidation of **7**, **8**, and **9** will be described later.

Scheme 1. A Possible Reaction Path for the Oxidation of Linalool (9) by the PCWP−H_2O_2 System



Although satisfactory results in the epoxidation of monoterpenes by the PCWP−H_2O_2 system in chloroform were obtained, the use of a chlorocarbon as the solvent is undesirable from environmental and industrial points of view.[9] Hence, we attempted to use nontoxic solvents other than chloroform, and it was found that *tert*-butyl alcohol is suitable for the epoxidation of terpenes by the present system. The oxidation of **1** with 35% H_2O_2 by PCWP in *tert*-butyl alcohol resulted in **1a** together with large quantities of cleaved products such as *vic*-diol. However, when a hydrogen peroxide solution of *tert*-butyl alcohol obtained by removing the water by treating with $MgSO_4$ prior to use was employed, the epoxidation was carried out with higher selectivity. Thus, **1** could be oxidized to **1a** in *tert*-butyl alcohol in 80% yield, and 1-octene (**11**), much less reactive than **1a**, was also found to be converted into 1,2-epoxyoctane (**11a**) under refluxing conditions in 76% yield (eqs 2 and 3).

$$\mathbf{1} + 1.1\,H_2O_2 \xrightarrow[t\text{-BuOH, 40 °C, 2 h}]{\text{PCWP (0.5 mol\%)}} \underset{80\ \%}{\mathbf{1a}} \qquad (2)$$



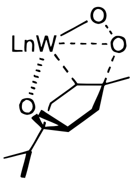
11

11a 76 %

Discussion

Although several oxidation systems have been developed for the epoxidation of terpenes, a variety of monoterpenes was oxidized with aqueous hydrogen peroxide by PCWP under biphase conditions to the corresponding mono- and diepoxide with good regio- and/or stereoselectivities. There are some differences in the selectivity of the terpene oxidation by the PCWP−H_2O_2 system compared with those by conventional methods.

γ-Terpinene (**2**) was converted into the diepoxide **2c** with high stereoselectivity (*cis*-**2c**/*trans*-**2c** = 95/5) by the present oxidation system (Table 1, run 4), while the epoxidation of **2** by *m*CPBA produced *trans*-**2c** rather than *cis*-**2c** (*cis*-**2c**/*trans*-**2c** = 30/70). In the epoxidation of **2a** and **2b** by the PCWP−H_2O_2 system, the peroxotungsten species seems to be favorable for approaching the double bond from the same plane where the oxirane ring is located, probably because of the neighboring effect of the oxygen atom. Similar neighboring effects are observed in the epoxidation of 8-*syn* and 8-*anti*-hydroxydicyclopentadienes by the heteropolyoxometalate−H_2O_2 system[12] and the oxidation of 3-cyclohexen-1-ol with *t*-BuOOH by $Mo(CO)_6$ or $VO(acac)_2$, where *syn*-3,4-epoxycyclohexan-1-ol was produced with high stereoselectivity (*syn*-epoxide/*anti*-epoxide = 98/2).[13]



Although linalool (**9**) is reported to be converted into 3,7-dimethyl-1,2-epoxy-6-octen-3-ol (**9d**) by $VO(acac)_2$[13] or $Ti(OPr^i)_4$[14] with *t*-BuOOH, the oxidation of **9** by the PCWP−H_2O_2 system produced about a 2:1 mixture of hydroxy furan **9a** and hydroxy pyran **9b** (Table 1, run 13). The vanadium or titanium hydroperoxo complexes generated by $VO(acac)_2$ or $Ti(OPr^i)_4$ and alkyl hydroperoxide are thought to coordinate to the hydroxy group of

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[12] Okabayashi, T.; Nishimura, T.; Matoba, Y.; Yamawaki, K.; Ishii, Y.; Hamanaka, S.; Ogawa, M. *J. Jpn. Petrol. Inst.* **1986**, *29*, 419.

[13] Sharpless, K. B.; Michaelson, R. C. *J. Am. Chem. Soc.* **1973**, *95*, 6136.

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9, and then the oxygen transfers to the allylic double bond to form **9d**. In contrast, the oxidation of **9** by the present system took place at the inner double bond rather than the allylic double bond. This finding indicates that the PCWP possesses higher electrophilicity than the vanadium and titanium complexes.[15]

Recently, Tomaselli and co-workers demonstrated the strong electrophilicity of the PCWP by spectroscopic studies.[16] They suggested that the remarkable electrophilic reactivity of polyoxoperoxo complexes such as PCWP, which are effective epoxidizing agents, in contrast to anionic simple peroxo complexes such as $MO(O_2)_2$-HMPT·H_2O (M = Mo, W), is due to a more effective charge delocalization in the former peroxo complexes. We have shown that the PCWP possesses a strong electrophilicity which can even epoxidize electron-deficient alkenes such as α,β-unsaturated ketones.[2g]

In order to explain the regioselectivity in the PCWP-catalyzed epoxidation of monoterpenes **1**−**9**, the HOMO coefficients of these substrates were calculated using the CAChe system (Table 2).[17] The eigenvectors in the HOMO of **1**−**9** were around −9 eV, and so the oxidation of all these substrates can occur under similar conditions (*i.e.*, at room temperature for several hours). The regioselectivity of the epoxidation of **1**−**9** by the PCWP−H_2O_2 system can be correlated with the frontier molecular orbital calculations. The carbon−carbon double bonds having the larger HOMO coefficient in **1**−**9** (except for **7** and **8**) were found to be preferentially oxidized, which indicates that the regioselectivity in the epoxidation of terpenes is dominated by the electron density of the double bonds.

Table 2. Frontier Orbital Coefficients of Various Monoterpenes

terpene	eigenvectors (eV)	coefficients	terpene	eigenvectors (eV)	coefficients
1	−9.299	C_1 0.58423	**6**	−9.634	C_2 0.03007
		C_2 0.62090			C_3 0.01870
		C8 0.10685			C_6 0.63525
		C9 0.12366			C_7 0.59314
2	−8.999	C_1 0.41516	**7**	−9.099	C_2 0.07121
		C_2 0.43447			C_3 0.06056
		C4 0.40056			C_6 0.62700
		C5 0.41897			C_7 0.59490
3	−9.297	C_2 0.23278	**8**	−9.330	C_2 0.14011
		C_3 0.24490			C_3 0.12343
		C_6 0.55871			C_6 0.57970
		C_7 0.53411			C_7 0.60718
4	−9.423	C_2 0.09402	**9**	−9.526	C_1 0.01294
		C_3 0.07805			C_2 0.01017
		C_6 0.61937			C_6 0.63186
		C_7 0.58931			C_7 0.59592
5	−9.517	C_2 0.02670			
		C_3 0.01427			
		C_6 0.63220			
		C_7 0.59366			

For example, in the substrate **2**, the C_1−C_2 double bond, having larger HOMO coefficients than the C_4−C_5 bond, was preferentially oxidized to form **2a** although there could be a steric influence (Table 1, run 3). The oxidation of neryl acetate **3** produced monoepoxide **3a** (56%) along with considerable amounts of diepoxide **3b** (33%), whereas geranyl acetate **4**, the geometric isomer of **3**, was converted into monoepoxide **4a** (86%) and diepoxide **4b** (11%) under the same reaction conditions (Table 1, runs 5 and 7). The higher regioselectivity for **4** could be reasonably explained by steric effects and by comparing the large differences in the HOMO coefficients between **3** and **4**. The coefficients of the C_2−C_3 double bond of **4** are somewhat smaller than those of the C_6−C_7 double bond of **4**, compared with those of **3**. Hence, the epoxidation of **4** seems to proceed with high selectivity at the C_6-C_7 double bond, in contrast to that of **3**.

In the case of terpenes **7** and **8**, the HOMO coefficients of the C_2−C_3 double bonds are much smaller than those of the C_6−C_7 positions, but the epoxidations of **7** and **8** took place at the C_2−C_3 double bonds. This is believed to be due to the coordination of the PCWP to the primary hydroxy groups of **7** and **8** taking place more easily than that to the tertiary hydroxy group of **9**. Therefore, the epoxidation of **7** and **8** proceeds *via* the coordination of the PCWP to the hydroxy group to form epoxy alcohols **7a** and **8a**, respectively.

In summary, a variety of monoterpenes was selectively oxidized with 35% H_2O_2 in the presence of a catalytic amount of PCWP to give the corresponding mono- and diepoxides in good yields under mild conditions. The regioselectivity of the present epoxidation of terpenes is rationally explained with MO calculations of the double bonds in the terpene molecules.

Experimental Section

General Procedures. All starting materials were commercially available and used without further purification. PCWP was prepared by the method reported previously.[2d] GC analysis was performed with a flame ionization detector using a 0.2 mm × 25 m capillary column (OV-1). ^{1}H- and ^{13}C-NMR were measured at 270 and 67.5 MHz, respectively, in $CDCl_3$ with Me_4Si as the internal standard. Infrared (IR) spectra were measured using NaCl pellets. GC-MS spectra were obtained at an ionization energy of 70 eV. The yields of products were estimated from the peak areas based on the internal standard technique.

General Procedure for the Oxidation of Terpenes. To a stirred solution of PCWP (41 mg, 0.5 mol %) and 35% H_2O_2 (4.4 mmol) in $CHCl_3$ (5 mL) was added terpene (4 mmol), and the reaction mixture was stirred at room temperature for 0.5−6 h. The reaction was quenched by adding water to the reaction mixture, and the products were extracted with dichloromethane. The extract was dried over anhydrous $MgSO_4$ and evaporated under reduced pressure. The products were purified by column chromatography on silica gel (hexane/ethyl acetate (10−3/1)). The compounds **2a**,[9] **2b**,[9] **2c**,[9] **3a**,[19] **3b**,[20] **4a**,[19] **4b**,[20] **5a**,[21] **7a**,[13] **8a**,[2i,13] **9a**,[22] **9b**,[22] and **9c**[13] were reported previously.

3,7-Dimethyl-6,7-epoxy-2-octenenitrile (6a): IR (NaCl) 2964, 2217, 1633, 1446, 1379, 1123, 798, 678 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 270 MHz) δ 5.19 (s, 1H), 2.76 (t, J = 6.3 Hz, 1H), 2.69 (dd, J = 5.0 and 7.6 Hz, 2H), 1.96 (s, 3H), 1.75−1.57 (m, 2H), 1.33 (s, 3H), 1.29 (s, 3H); δ 5.19 (s, 1H), 2.57 (t, J = 7.6 Hz, 1H), 2.36 (dd, J = 7.3 and 15.2 Hz, 2H), 2.09 (s, 3H), 1.85−1.71 (m, 2H), 1.32 (s, 3H), 1.28 (s, 3H); ^{13}C-NMR ($CDCl_3$, 67.8

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[17] The geometries of **1**−**9** were calculated by the PM3 semiempirical method[18] as implemented in the MOPAC version 6.10 system. The calculation was performed twice to localize the two double bonds of the monoterpenes into the XY plane.

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MHz) δ 164.1, 163.9, 116.7, 116.5, 96.2, 95.6, 62.9, 62.9, 58.3, 58.2, 35.3, 32.9, 26.9, 26.4, 26.2, 24.5, 20.8, 18.5, 18.4.

Procedure for the Epoxidation of 1 in *tert*-Butyl Alcohol. To a stirred solution of 35% H_2O_2 (9 mmol) in *t*-BuOH (15 mL) was added anhydrous $MgSO_4$ (1.5 g), and the suspended solution was stirred at room temperature for 0.5 h and filtered. To the filtrate were added PCWP (62 mg, 0.5 mol %) and **1** (6 mmol), and the mixture was stirred at 40 °C for 2 h. The workup was performed by the same method as described above.

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Supporting Information Available: Copies of NMR spectra (26 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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