

## Catalytic oxidation of $\alpha$ -pinene by transition metal using *t*-butyl hydroperoxide and hydrogen peroxide

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### Abstract

The allylic oxidation of  $\alpha$ -pinene **1** was investigated using various catalytic systems. By a proper choice of the latter, the reaction can be directed toward the selective synthesis of verbenol **2** or verbenone **3**. High yield into verbenone was achieved under mild conditions with copper salts as catalysts and *t*-butyl hydroperoxide (TBHP) as oxidant. On the other hand, when Pd(acac)<sub>2</sub> was used with hydrogen peroxide, verbenol was obtained as the main product.

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### 1. Introduction

The allylic oxidation of terpenic olefins can constitute an important transformation reaction of these cheap, natural products, into their corresponding oxygenated compounds which are largely applied in organic synthesis. Indeed, oxygenated derivatives are precursors for a number of pharmaceutical, perfume and flavor synthesis [1,2]. However, a limited number of investigations on this subject have been reported, whereas the selective conversion of this class of olefins to functionalized compounds is crucial for their valorization. Until now, non-catalytic oxidation of terpenes generally takes place with poor reproducibility and low yields and selectivities [3–6]. On the other hand, the oxidation of non-terpenic olefin

catalyzed by various transition metal complexes in the presence of a wide range of oxidizing agents such as molecular oxygen [5,6], hydrogen peroxide [7], *t*-butylhydroperoxide (TBHP) [8–11] and other oxygen donor agents [12,13] has been reported by several authors. As far as we are concerned, we have previously reported that the functionalization of limonene performed in the presence of a Pd<sup>II</sup>–Cu<sup>II</sup> catalytic combination selectively produces either esters, ethers, alcohols ... according to the reaction conditions [13–15]. In line with our continuous interest in this field, we report here the result of our investigations on the oxidation of  $\alpha$ -pinene **1** in the presence of various catalytic systems, using tertibutyl hydroperoxide or hydrogen peroxide as oxidizing agents.<sup>1</sup>

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<sup>1</sup> For recent papers on  $\alpha$ -pinene oxidation, see [16–19].

## 2. Results and discussion

### 2.1. Selective synthesis of verbenone

In order to select the more efficient catalytic system toward the formation of verbenone **3**, a screening of various salts of copper, palladium, manganese and cobalt, usually reported as oxidation catalysts, was made under various conditions with commercial 70% aqueous *t*-BuOOH as oxidant and MeCN as solvent [20,21]. The results obtained are summarized in Table 1. In the absence of catalyst and under either nitrogen or oxygen (entries 1–3), as expected, the activity was low and initially practically only peroxides **4** and **5** (see Scheme 1) were obtained in moderate yields. At longer reaction time, small amounts of verbenol **2** and verbenone **3** were also detected together with a decrease of peroxide **5** whereas the amount of **4** remained constant (entries 1 and 2). Under nitrogen, addition of a catalyst slightly enhanced the activity and the selectivity toward **2** and **3** (entries 4–8) except Pd(OAc)<sub>2</sub> which was inactive toward the formation of these compounds but increased the amount of **4** (entry 6), and CuI which markedly enhanced the conversion (entry 4). Therefore, further investigations were made with this last catalyst. The nature of the gas phase appeared to have a great influence on the reaction. Actually, when the reaction was performed

under air instead of nitrogen, the selectivity into verbenone increased to the detriment of **4** and **5**. Substitution of air by oxygen induced a further increase of both activity and selectivity toward verbenone and this increase was even more significant when O<sub>2</sub> was bubbled through the reaction medium during the course of the reaction (entry 11).

It appears from these results that verbenone formation is a catalytic process related to the use of dioxygen, about which two roles could be assigned: it can either be involved in the direct production of verbenone or only promote its formation from peroxide **5**.

In this context Barton and Wang have already shown in the oxidation of fluorene by GoAgg<sup>v</sup> system that fluorenone was formed from fluorenyl *t*-butylperoxide under argon, whereas under air, fluorenone was directly produced. Hence the reaction intermediates could react with oxygen in air to give the ketone and with TBHP to give the peroxide [11].

In order to gain a better insight on this point, a kinetic study was carried out under nitrogen using CuI as catalyst. Fig. 1, which depicts the evolution of peroxide **5** and verbenone versus time, shows that **5** was formed immediately. This compound reached a maximum after 1 h (67%) and then disappeared in favor of verbenone whose amount, insignificant at the early stage of the reaction, rapidly increased after the first hour and then much more slowly after 4–5 h (only a

Table 1  
Oxidation of  $\alpha$ -pinene catalyzed by different transition metal salts

Entry	Catalyst	Atmosphere	Time (h)	Conversion (%)	Selectivity(%) <sup>a,b</sup>					
					<b>2</b>	<b>3</b>	<b>4</b>	<b>5</b>	<b>6</b>	<b>8</b>
1	None	N <sub>2</sub>	24	52	tr <sup>c</sup>	tr	31	54	tr	tr
2	None	N <sub>2</sub>	48	80	1	6	31	48	tr	tr
3	None	O <sub>2</sub>	24	68	3	6	23	40	tr	tr
4	CuI	N <sub>2</sub>	10	98	5	19	26	40	3	3.5
5	Cu(OAc) <sub>2</sub>	N <sub>2</sub>	48	86	3	15	28	43	tr	tr
6	Pd(OAc) <sub>2</sub>	N <sub>2</sub>	48	72	4	6	45	31	tr	4
7	Mn(acac) <sub>2</sub>	N <sub>2</sub>	48	82	4	12	30	45	tr	3
8	Co(acac) <sub>3</sub>	N <sub>2</sub>	28	98	3	14	31	42	2	4
9	CuI	Air	9	98	3	36	24	31	3.5	3
10	CuI	O <sub>2</sub>	7	97	2	41	21	21	3	1
11	CuI <sup>d</sup>	O <sub>2</sub>	2	100	6.5	54	19	20.5	tr	tr

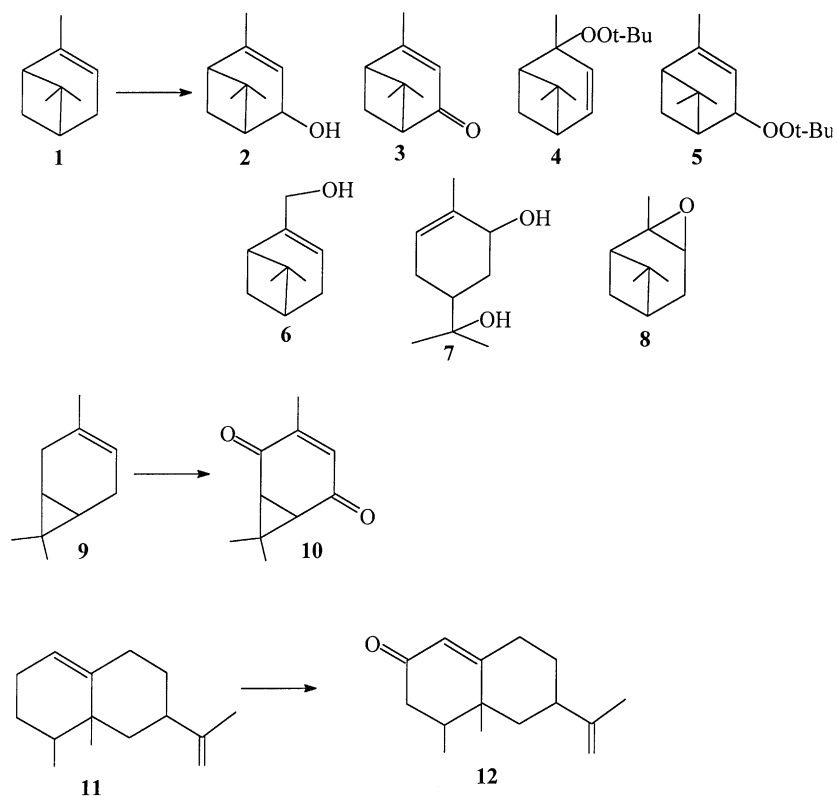
Conditions:  $\alpha$ -pinene (7.3 mmol); catalyst (0.073 mmol); *t*-BuOOH (44 mmol); MeCN (6 ml); *T* = 50 °C, TBHP was added at once.

<sup>a</sup> Determined by GC and based on reacted  $\alpha$ -pinene.

<sup>b</sup> Small amounts of unidentified products are also detected.

<sup>c</sup> Trace amounts.

<sup>d</sup> O<sub>2</sub> bubbling.



Scheme 1.

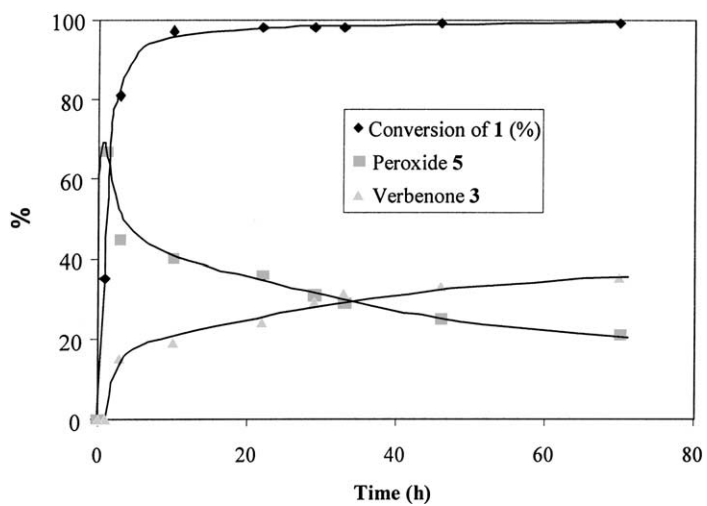


Fig. 1. Oxidation of  $\alpha$ -pinene catalyzed by CuI; conversion and product distribution vs. time. Conditions:  $\alpha$ -pinene = 7.3 mmol, CuI = 0.073 mmol, TBHP = 6 eq., MeCN = 6 ml, 50 °C, under nitrogen.

Table 2  
Temperature effect on the oxidation of  $\alpha$ -pinene catalyzed by CuI

Entry	$T$ ( $^{\circ}\text{C}$ )	Time (h)	Conversion (%)	Selectivity (%) <sup>a</sup>					
				<b>2</b>	<b>3</b>	<b>4</b>	<b>5</b>	<b>6</b>	<b>8</b>
1	0–20 <sup>b</sup>	24	91	21	40	5	9	12	0.4
2	35	26	96	14	52	4	6	11	7
3	70	11	100	tr <sup>c</sup>	70	7	5	8	3

Conditions: same as in Table 1; O<sub>2</sub> bubbling.

<sup>a</sup> Determined by GC.

<sup>b</sup> Addition of TBHP to a stirred solution of  $\alpha$ -pinene and catalyst in MeCN cooled at 0  $^{\circ}\text{C}$  (ice bath) was done dropwise (6h); the reaction mixture was allowed to react at room temperature for 18 h.

<sup>c</sup> Trace amounts.

20% conversion enhancement was observed between 10 and 70 h of reaction time). This observation proves that peroxide **5** behaves in the presence of CuI as an intermediate that reacts to give the ketone **3**, whereas it remains stable in the absence of catalyst. As the reaction proceeds in acetonitrile and as nitriles are known to form peroxyimidic acids, the formation of peroxides **4** and **5** in the absence of catalyst is probably due to an homolytic cleavage of the O–H bond of TBHP initiated by these peroxyimidic acids, giving  $t\text{-BuOO}^{\bullet}$  radicals which react with the substrate after hydrogen abstraction [22].

Moreover, the fact that the transformation of **5** into **3** was fast at the early stage of the reaction (i.e. with fresh  $t\text{-BuOOH}$ ) and then slowed down at longer reaction time, prompted us to add  $t\text{-BuOOH}$  dropwise during the whole reaction time instead of adding this reagent at once. In the same way, in order to further optimize the reaction conditions, the influence of temperature was also checked. This slow addition of  $t\text{-BuOOH}$  associated with an increase in temperature led to an increase in verbenone selectivity (Table 2). Actually, when the reaction was performed at 70  $^{\circ}\text{C}$ , verbenone **3** was obtained with a 70% selectivity (entry 3). Lower temperatures led to a decrease in verbenone formation on behalf of verbenol that was obtained with 14 and 21% selectivities when the reaction was run at 35 and 20  $^{\circ}\text{C}$ , respectively. This result shows that higher temperatures promote the transformation of the intermediate into the ketone instead of the alcohol.

Finally, taking into account these results, different catalysts were tested under the best conditions described above. In the same way, for comparison, the efficiency of the other catalysts initially used was also checked. Table 3, which summarizes the main results,

confirms that copper salts are again the most suitable. However, the product distribution was not only strongly influenced by the nature of the metal but also by its oxidation state as well as by the nature of the counter anion. Indeed when CuCl was used in place of CuI the selectivity into verbenone only reached 45% (entry 2); on the other hand, using CuCl<sub>2</sub>, a 78% selectivity was obtained (entry 3).

It should also be noted, although the results are not reported in Table 3, that when TBHP was substituted by H<sub>2</sub>O<sub>2</sub> with CuI or CuCl<sub>2</sub> as catalyst, the reaction occurred with poor activity (25% conversion after 48 h) and selectivity. A great number of unidentified products were obtained with probably opening of the cyclobutane ring.

Interestingly, the use of palladium gave rise to the formation of significant amounts of verbenol **2** with both TBHP and more markedly H<sub>2</sub>O<sub>2</sub> (Table 3, entries 7–9). The following section will therefore be concerned with attempts at the selective synthesis of this compound.

## 2.2. Synthesis of verbenol

Fig. 2 shows the effect of varying the Pd amount on the oxidation of  $\alpha$ -pinene in the presence of H<sub>2</sub>O<sub>2</sub> as oxidant. An increase in Pd(acac)<sub>2</sub> concentration enhanced not only the conversion but also significantly the formation of **2**. Indeed, while the selectivity into verbenol did not exceed 41% for a substrate/Pd ratio of 100, it reached 78% when this ratio decreased to 25. It is also noteworthy that as in the case of TBHP, slow addition of H<sub>2</sub>O<sub>2</sub> is needed otherwise its accumulation in the reaction medium induces the precipitation of Pd black and consequently inhibited the reaction.

Table 3  
Oxidation of  $\alpha$ -pinene under optimized conditions

Entry	Catalyst	Time (h)	Conversion (%)	Selectivity (%) <sup>a</sup>							
				2	3	4	5	6 <sup>b</sup>	7	8	
1	CuI	11	100	tr	70	7	5	8	0	3	
2	CuCl	12	98	1	45	2	3	6	9	3	
3	CuCl <sub>2</sub>	12	100	3	78 (71)	3	4	2	9	1	
4	Cu(OAc) <sub>2</sub>	17	100	tr	60	4	4	7	0	4	
5	Co(OAc) <sub>2</sub>	12	98	2	43	3	3	5	3	4	
6	Mn(OAc) <sub>2</sub>	46	100	tr	48	3	6	3	6	4	
7	Pd(OAc) <sub>2</sub>	26	92	7	26	16	14	2	tr <sup>c</sup>	6	
8	Pd(acac) <sub>2</sub>	22	94	10	30	4	5	3	tr	11	
9	Pd(acac) <sub>2</sub> <sup>d</sup>	21	86	41	12	0	0	2	tr	13	

Conditions:  $\alpha$ -pinene (7.3 mmol); catalyst (0.073 mmol); *t*-BuOOH (44 mmol); MeCN (6 ml);  $T = 70^\circ\text{C}$ ; O<sub>2</sub> bubbling.

<sup>a</sup> Determined by GC, the number into brackets refers to the isolated yield of the corresponding product with a purity >95%.

<sup>b</sup> A standard sample of myrtenol was used to determine this compound.

<sup>c</sup> Trace amounts.

<sup>d</sup> H<sub>2</sub>O<sub>2</sub> (30%, 6 eq.) was used in place of *t*-BuOOH under air.

A study of the influence of the nature of the Pd precursor is reported in Table 4. Among the Pd compounds tested, Pd(acac)<sub>2</sub> appears the more suitable; the order of catalytic efficiency to promote the formation of verbenol is as follows: Pd(acac)<sub>2</sub> > Pd(OAc)<sub>2</sub>  $\gg$  PdCl<sub>2</sub>  $\approx$  PdBr<sub>2</sub>. The use of PdX<sub>2</sub> (X: Cl, Br) as catalyst leads to the formation of a great range of by products which have not been identified because of their low concentration in the reaction medium.

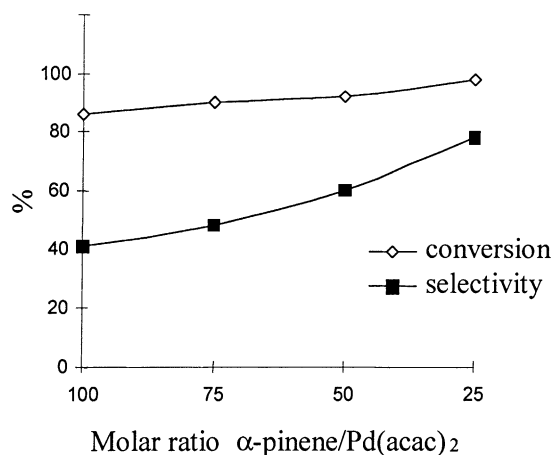


Fig. 2. Oxidation of  $\alpha$ -pinene with the system Pd(acac)<sub>2</sub>-H<sub>2</sub>O<sub>2</sub>; conversion and verbenol selectivity vs. molar ratio of Pd(acac)<sub>2</sub>. Conditions:  $\alpha$ -pinene = 7.3 mmol, H<sub>2</sub>O<sub>2</sub> (30%) = 6 eq., MeCN = 6 ml, 70 °C, 21 h, under air.

The palladium-catalyzed oxidation of olefins with H<sub>2</sub>O<sub>2</sub> has been the subject of numerous synthetic and mechanistic investigations [23–26]. In the case of terminal olefin giving saturated ketones, the involvement of a palladium hydroperoxide A-Pd-OOH (A: OAc, acac) which undergoes an oxygen transfer to the olefin via a pseudocyclic peroxypalladium mechanism is generally accepted [25,26]. On the other hand, the selective formation of allylic alcohols by oxidation of various  $\pi$ -allyl palladium complexes was reported [27]. Thus as such  $\pi$ -allylic palladium complexes are easily formed from terpenic olefins [13,14], the formation of verbenol with the Pd-H<sub>2</sub>O<sub>2</sub> system proceeds probably via a mechanism involving such species.

### 2.3. Oxidation of other terpenes

In order to delineate the scope and limitations of the procedure described above, the optimised conditions based on both copper or palladium catalysts were applied to different terpenic olefins. The activity and the selectivity were strongly dependent on the substrate structure. Thus, the oxidation of limonene occurred with high activity but poor selectivity. Numerous unidentified products were formed. This result is probably related to the high reactivity of this substrate previously encountered in other reactions [12]. The oxidation of 3-carene **9** with the system CuI-TBHP-O<sub>2</sub>

Table 4  
Oxidation of  $\alpha$ -pinene with the palladium–H<sub>2</sub>O<sub>2</sub> system

Entry	Catalyst	Time (h)	Conversion (%)	Selectivity (%) <sup>a</sup>				
				2	3	6	7	8
1	Pd(OAc) <sub>2</sub>	34	94	60	11	5	tr <sup>b</sup>	5
2	Pd(acac) <sub>2</sub>	21	98	78 (70)	2	1	tr	8
3	PdCl <sub>2</sub>	22	98	4	13	7	tr	8
4	PdBr <sub>2</sub>	20	100	4	15	6	tr	tr

Conditions:  $\alpha$ -pinene (7.3 mmol); catalyst (0.29 mmol); H<sub>2</sub>O<sub>2</sub> (44 mmol); MeCN (6 ml); T = 70 °C.

<sup>a</sup> Determined by GC, the number into brackets refers to the isolated yield of the corresponding product.

<sup>b</sup> Trace amounts.

afforded the diketone **10** as the main product (93% conversion after 7 h, 55% selectivity). Finally, the oxidation of valencene **11**, with the same catalytic system, led to nootkatone **12** with high activity (100% conversion after 4 h) and good selectivity (80%). Conversely, upon using the Pd–H<sub>2</sub>O<sub>2</sub> system, only poor results were obtained with the different substrates.

#### 2.4. Conclusion

Systematic investigations on the nature of the catalyst, the oxidizing agent and the reaction conditions have allowed us to develop two performing systems for the allylic oxidation of  $\alpha$ -pinene. Actually, the Cu–TBHP–O<sub>2</sub> combination leads to verbenone with high yield whereas the use of the Pd–H<sub>2</sub>O<sub>2</sub> leads to the selective formation of verbenol. In both cases, a dropwise addition of the oxidant (TBHP or H<sub>2</sub>O<sub>2</sub>) is needed to obtain high yields into the desired product. The addition of TBHP at once induces the formation of peroxidic compounds while that of H<sub>2</sub>O<sub>2</sub> leads to its rapid decomposition and precipitation of inactive palladium black.

Finally the generalization of the reaction to others terpenes appears easy in the case of the Cu–TBHP–O<sub>2</sub> combination but using Pd–H<sub>2</sub>O<sub>2</sub> system would require further improvement to obtain good yields and selectivities into the corresponding alcohol.

### 3. Experimental

#### 3.1. Apparatus and chemicals

All reagents and solvents were purchased from commercial sources (Aldrich, Acres) and used as received.

The reaction mixture were analysed on a Delsi 3000 series chromatograph equipped with an FID detector, using silica capillary columns CPSil5CB (10 m × 0.33 mm, Chrompack) or B.P.20 (25 m × 0.25 mm, SGE).

Liquid chromatographies were performed on silica gel (Merck 60, 220–440 mesh; eluents: hexane–AcOEt). <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded at 200 MHz (Bruker Model AM 200) using CDCl<sub>3</sub> as the solvent and SiMe<sub>4</sub> as the internal standard.

#### 3.2. General procedure for oxidation of terpenic olefins with tert-butyl hydroperoxide as oxidant

A mixture of catalyst (0.073 mmol) and olefin (7.3 mmol) in 6 ml of acetonitrile, in a three-necked flask equipped with a cooled condenser and a dropping funnel, was stirred for 10 min. To this solution was added a 70% aqueous solution of TBHP (44 mmol) in 4 ml of acetonitrile during 7 h. Oxygen was gently bubbled through the solution. The mixture was stirred for the reported reaction time at 70 °C. The progress of the reaction was followed by GC. When the reaction was stopped, 5 ml of water were added and the resulting mixture was extracted four times with 10 ml of ether (1:1), the combined organic phases were dried over MgSO<sub>4</sub>, and evaporated under reduced pressure. The reaction products were then isolated by column chromatography on silica using various ratios of *n*-hexane/AcOEt.

#### 3.3. Addition of TBHP at once

In a Schlenk tube, the catalyst (0.073 mmol) was dissolved in 6 ml of acetonitrile under nitrogen, 7.3 mmol of  $\alpha$ -pinene and 70% solution of TBHP

(44 mmol) were added. The mixture was stirred for the reported time at the indicated temperature; when the reaction was achieved, the same procedure as described above was used for the purification of the products.

### 3.4. General procedure for oxidation of terpenic olefins with $H_2O_2$ as oxidant

The catalyst (0.29 mmol) dissolved in 6 ml of acetonitrile and the olefin (7.3 mmol) were placed in a two-necked flask, equipped with a cooling condenser and a dropping funnel. Then to this solution hydrogen peroxide (30%; 44 mmol) was added dropwise at 70 °C during 4 h. The resulting mixture was stirred for the indicated time. Pure products were isolated by column chromatography of the crude material on silica gel using various ratios of hexane–AcOEt as the eluent.

The structure of the isolated products was established unambiguously by  $^1H$  and  $^{13}C$  NMR spectroscopies by comparison of the data with those reported in the literature.

**Verbenol 2:**  $CDCl_3$ ,  $\delta$  (ppm); NMR  $^1H$ : 0.85 (3H, s,  $CH_3$ , 8-H); 1.31 (3H, s,  $CH_3$ , 10-H); 1.71 (t,  $J = 1.59$  Hz,  $CH_3$ , 9-H); 2.00 (m, 1H, 4-H); 2.17 (m, 1H, 5-H); 2.26 (m, 1H, 6-H); 4.43 (m, 1H, 1-H); 5.32 (m, 1H, 2-H). NMR  $^{13}C$ : 20.40 (C8); 22.62 (C9); 26.62 (C10); 28.62 (C5); 46.25 (C6); 47.98 (C7); 48.13 (C4); 70.47 (C1); 118.80 (C2); 148.84 (C3). The NMR data corresponded with the published data [17].

**Verbenone 3:**  $CDCl_3$ ,  $\delta$  (ppm); NMR  $^1H$ : 0.98 (3H, s,  $CH_3$ , 8-H); 1.47 (3H, s,  $CH_3$ , 10-H); 1.98 (d,  $J = 1.65$  Hz,  $CH_3$ , 9-H); 2.39 (td, 1H,  $J_1 = 6.36$  Hz,  $J_2 = 1.59$  Hz, 4-H); 2.63 (td, 1H,  $J_1 = 6.67$  Hz,  $J_2 = 1.27$  Hz, 6-H); 2.78 (dt, 1H,  $J_1 = 8.9$  Hz,  $J_2 = 5.4$  Hz, 5-H); 5.70 (m, 1H, 2-CH). NMR  $^{13}C$ : 22.09 (C8 ou C9); 23.51 (C10); 26.56 (C9 ou C8); 40.83 (C5); 49.74 (C6); 54.03 (C7); 57.59 (C4); 121.16 (C2); 170.11 (C3); 204.02 (C1). In accordance with [17].

**Peroxide 4:**  $CDCl_3$ ,  $\delta$  (ppm); NMR  $^1H$ : 1.00 (3H, s,  $CH_3$ , 8-H); 1.24 (9H, s, *t*-Bu); 1.40 (3H, s,  $CH_3$ , 10-H); 1.44 (3H, s,  $CH_3$ , 9-H); 1.82 (d, 1H,  $J = 8.26$  Hz, 5-H); 2.22 (q, 1H,  $J = 5.72$  Hz, 4-H); 2.28 (m, 1H, 6-H); 2.34 (m, 1H, 5-H); 5.54 (dm, 1H,  $J = 8.6$  Hz, 2-H); 6.38 (dd, 1H,  $J_1 = 6.3$  Hz,  $J_2 = 5.7$  Hz, 3-H). NMR  $^{13}C$ : 22.4 (C8); 24.23 (C9); 26.89 (*t*-Bu); 27.73 (C10); 32.57 (C5); 42.65 (C4); 50.52 (C6); 46.47 (C7);

78.38 (C11); 83.67 (C1); 126.71 (C2); 139.86 (C3). The NMR data corresponded well with the reported data [28].

**Peroxide 5:**  $CDCl_3$ ,  $\delta$  (ppm); NMR  $^1H$ : 0.90 (3H, s,  $CH_3$ , 8-H); 1.27 (9H, s, *t*-Bu); 1.37 (3H, s,  $CH_3$ , 10-H); 1.75 (3H, t,  $J = 1.58$  Hz,  $CH_3$ , 9-H); 1.44 (d, 1H,  $J = 8.67$  Hz, 5-H); 2.04 (td, 1H,  $J_1 = 5.72$  Hz,  $J_2 = 1.28$  Hz, 4-H); 2.25 (dt, 1H,  $J_1 = 8.9$  Hz,  $J_2 = 5.72$  Hz, 5-H); 2.48 (m, 1H, 6-H); 4.56 (m, 1H, 1-H); 5.33 (m, 1H, 2-H). NMR  $^{13}C$ : 20.51 (C8); 22.97 (C9); 26.76 (C10); 26.58 (*t*-Bu); 28.92 (C5); 43.07 (C6); 45.85 (C7); 48.03 (C4); 79.78 (C11); 82.33 (C1); 114.06 (C2); 151.21 (C3). The NMR data corresponded well with the reported data [28].

**Sobrerol 7:**  $CDCl_3$ ,  $\delta$  (ppm); NMR  $^1H$ : 1.16 et 1.20 (2s, 6H); 1.31–1.47 (m, 1H); 1.77 ( $CH_3$ , 10); 1.97–2.18 (m, 2H); 4.01–4.04 (m, 1H); 5.53–5.56 (m, 1H); 20.51 ( $CH_3$ ); 26.21 (C9); 27.21 (C8); 27.74 (C4); 32.66 (C6); 38.84 (C5); 68.62 (C1); 72.23 (C7); 125.25 (C3); 134.45 (C2). The values were in accordance with those published [17,29].

**Diketone 10:**  $CDCl_3$ ,  $\delta$  (ppm); NMR  $^1H$ : 1.29 (s,  $CH_3$ ); 1.30 (s,  $CH_3$ ); 2.31 (1H, 1CH); 2.36 (1H, 1CH); 1.94 (s,  $CH_3$ ); 6.50 (1H, =CH). NMR  $^{13}C$ : 15.41 (C8 or C9); 16.15 (C8 or C9); 29.05 (C10); 33.47 (C7); 38.95 (C5 or C6); 39.80 (C6 or C5); 137.63 (C2); 149.95 (C3); 194.30 and 194.93 (C1–C4). In accordance with [17].

**Nootkatone 12:**  $CDCl_3$ ,  $\delta$  (ppm); NMR  $^1H$ : 0.93 (d,  $CH_3$ ); 1.09 (s,  $CH_3$ ); 1.75 (s,  $CH_3$ ); 4.70 (d, = $CH_2$ ); 5.74 (s, =CH). NMR  $^{13}C$ : 14.86; 16.80; 20.77; 29.64; 31.56; 32.97; 39.26; 40.25; 40.39; 43.85; 109.20; 124.63; 149.03; 170.51; 199.63. In accordance with [30].

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