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# Role of organic solvent and influence of oxidant in the oxidation of linalool catalyzed by molybdenum and vanadium complexes

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## ABSTRACT

The coordination complexes  $[\text{MoO}_2(\text{SAP})_2]$  [Mo] and  $[\text{VO}(\text{SAP})_2\text{O}]$  [V] (SAP = salicylideneamino-phenolato) were tested as pre-catalysts for oxidation of a biomass-issued substrate, linalool (L). The reaction was studied using different oxidants, TBHP (in water or in decane) or  $\text{H}_2\text{O}_2$  (in water with/without acetonitrile). Efficient linalool (L) conversions were obtained with selectivity towards two selected products, 2-(5-methyl-5-vinyltetrahydro-furan-2-yl) propan-2-ol (1) and 2,2,6-trimethyl-6-vinyltetrahydro-2H-pyran-3-ol (2) depending on pre-catalysts and oxidant. Green metrics have been calculated and showed the role of organic solvent for the process.

## 1. Introduction

From the beginning of 20th century, cheap and highly available fossil ores became primary source of chemicals [1] but cheap fossil ores are depleting and there is urgent need to find new ores of raw chemicals [2]. Solutions have to be proposed to face fossil resource depletion, to preserve biodiversity and to fight against global warming [3]. One alternative to replace fossil resources is renewable biomass [4]. Biomass can bring a diversity of raw chemicals used for sophisticated compounds as sustainable versions of the fossil-based plastics and fuels, chemicals being partially responsible of pollution on our planet. [2] Twenty-five years ago, academics gathered those sustainable aspects into 12 Principles of Green Chemistry [5]. Among them, biomass is one important point but catalysis plays a crucial role to develop atom-economic and energy-saving industrial chemical process. Indeed, concerted use of biomass and catalysis can produce fine chemicals through sustainable, cleaner and safer methods [6,7]. As an example, reducing the use of organic solvent (especially those from fossil origin) can reduce the environmental threat, *de facto* increasing the sustainability of a chemical process [8]. Within the huge number of chemical reactions, oxidation lead to novel molecules and materials [9]. Former methods used oxidizing agents in high quantity ( $\text{CrO}_3$ ,  $\text{NaClO}$ , *m*-CPBA ...) that generated a high quantity of waste. Recent catalyzed and non-catalyzed oxidation methods use greener oxidants ( $\text{H}_2\text{O}_2$ , *t*BuOOH,  $\text{O}_2$ ), leading to minimal waste with high E-Factor [10]. Due to their importance in industry [11], efficient oxidation reactions with interesting E factor and low waste involve catalysis [12]. Thus, methods using active

metal-based catalysts and smoother oxidation agents have been investigated. Historically, metal complexes containing Pt, Pd, Ru, Ir, and Rh were the most effective in alcohol oxidation, but those metals had high price and low availability as drawbacks [13]. Other V- and Mo- containing metal-complexes have been developed. Being the second most abundant metal in the sea water [14], vanadium is interesting for its activity in haloperoxidases and nitrogenases processes [15] and for oxidation catalysis [16] since this metal has the ability to activate benign oxidants as peroxide or dioxygen [17]. Commonly employed in industrial processes, molybdenum is well recognized for (ep)-oxidation processes [18,19]. Mo- and V- containing Schiff base complexes have been found to be active oxidation catalysts of olefins [20], sulfides [21] or alcohols [22]. We are involved into (ep)oxidation processes using active (pre)catalysts (Mo-, V- or W- based) under greener conditions [23]. With the aim of reducing the amount of harmful and polluting substances in a chemical process, activity of those metal-catalysts with tridentate ligands has been reported for organic solvent-free (ep) oxidation of some olefins and alcohols, from simple fossil-based olefins as cyclooctene [24,25] and cyclohexene [26] to terpenic compounds as carveol [27], limonene [28], himachalenes [29], norlignanes [30] and lignanes [31].

Terpenic alcohols are natural substrates useful for the syntheses of chemicals [32,33] Used itself in food and pharmaceutical industries, linalool (L) can be a reagent for the synthesis of fine chemicals, perfumes, and agrochemicals [34]. Oxidation of L and subsequent cyclisation creates chiral heterocycles 2,2,6-trimethyl-6-vinyl-tetrahydro-2H-pyran-3-ol (1) and 2-(5-methyl-5-vinyl-tetrahydrofuran-2-yl) propan-

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2-ol) (2), biologically active species [35] valuable for drug synthesis [36–38]. Both tetrahydrofuranes and tetrahydropyrans building blocks are needed in the total synthesis of natural products with potential use in medicine, like lasonolide A [39], bryostatin 1 and eribulin [40], and phorboxazoles [36,41] (Fig. 1).

Both 1 and 2 could be obtained from 1,5-diene precursors [35], from dihydroxyallenes [37] or starting from L but with tedious synthetic pathways [38] not in agreement with Green Chemistry principles, including huge quantity of waste.

The cyclic oxide 1 can be produced from different substrates, using dihydroxyallenes cycloisomerization from propargyl oxirane (Scheme 1) [42], or intramolecular anodic coupling reactions [43]. 1 has been also described to be a precursor for the synthesis of the key flavor of hop oil, Karahanaenone [44]. Palladium-catalyzed formation of 1 and 2 can be done from geraniol (Scheme 2) [45].

More generally, 2,5-substituted tetrahydrofurans exhibited biological and anticancer properties [41,48] and tetrahydrofurans building blocks from  $\delta,\epsilon$ -unsaturated alcohols received considerable attention [49]. Formation of those cycles can be obtained through 5-hexenol ring closure [46] or reaction of homoallylic alcohols with aldehydes [50]. In the last few years, transition metal catalyzed oxidations [51] using primary oxidants like hydrogen peroxide [22], peroxy compounds [47] or molecular oxygen [52] showed easier pathways to obtain such building-blocks.

The cyclic oxides 1 and 2 can be synthesized directly from L through different methods. All conditions and results are summarized in Table S1. Historically, the first methods employed peracetic acid [53] or *m*-CPBA [54,55] in dichloromethane. Those efficient procedures suffered from tedious workup, high quantity of waste and, not the least, the use of chlorinated toxic solvent to be avoided [56]. After those discoveries, catalysis was employed with some metals. Heterocycles 1 and 2 were thus synthesized from L and  $H_2O_2$  as oxidant using the Ishii-Venturello W-containing catalyst and organic solvents within different conditions, under homogeneous conditions with the catalysts formed *in situ* [57] or previously prepared [58], or under heterogeneous

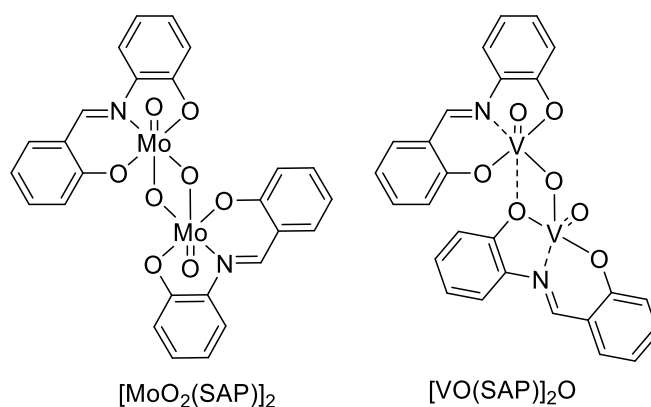
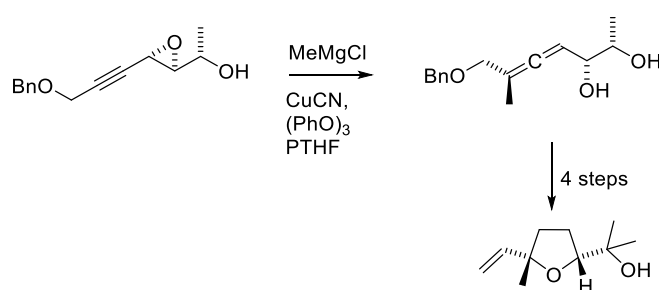


Fig. 2. Structure of metal complexes  $[MoO_2(SAP)]_2$  Mo and  $[VO(SAP)]_2O$  V used as pre-catalysts.



Scheme 1. Synthesis of 1 from propargyl oxirane [46].

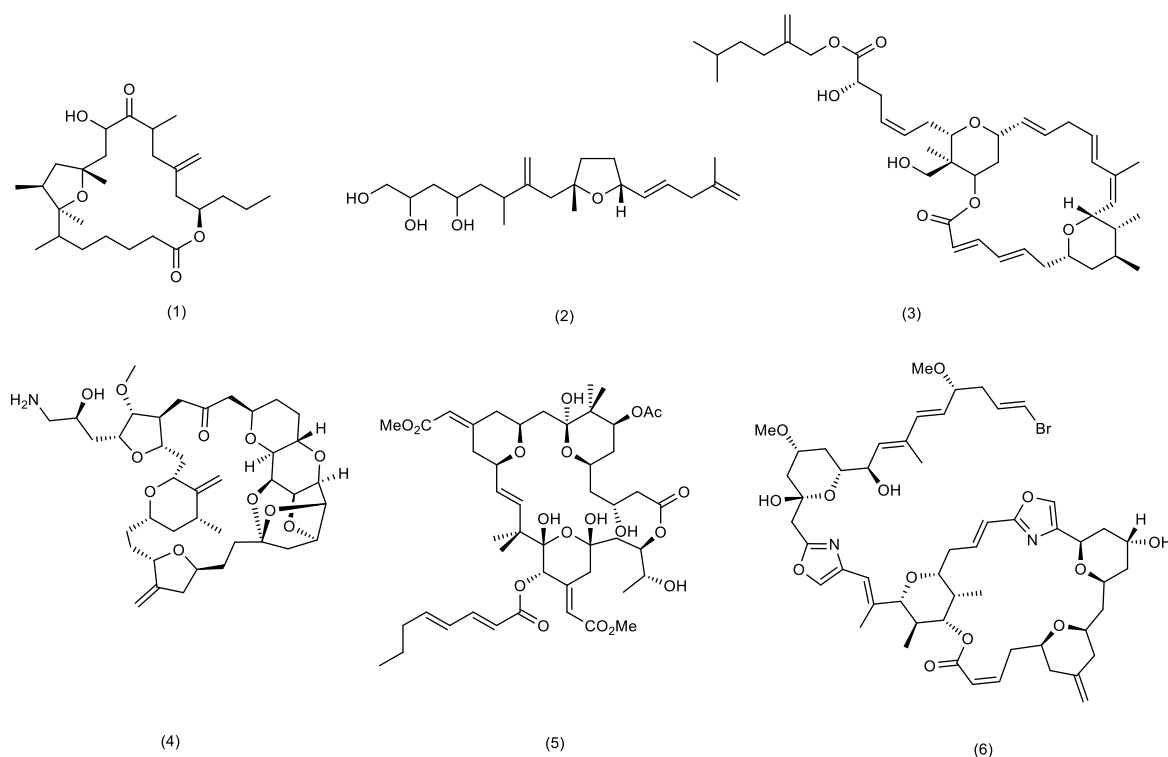
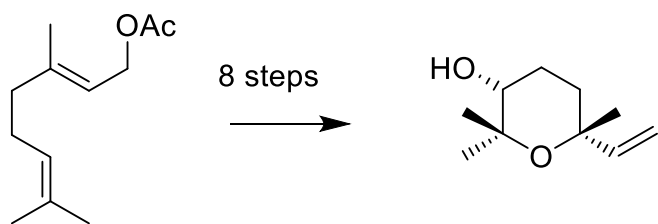


Fig. 1. General structures of natural products containing tetrahydrofuran and/or tetrahydropyran moieties: amphidinolides (1), amphidin A (2), lasonolide A (3), eribulin (4) bryostatin 1 (5) and Phorboxazole A (6).



Scheme 2. Synthesis of **2** from geranyl acetate [47].

conditions once the catalyst immobilized in amberlyst resin [59]. Titanium element was also used. Ti could be included within robust mesoporous objects, using CH<sub>3</sub>CN as solvent, H<sub>2</sub>O<sub>2</sub> as oxidant with Ti-beta and Ti-MCM-41 [60] or several type of oxidants with Ti-Al-beta [61]. Molecular Ti-containing species were used, less stable, some containing Cp ligands, using TBHP in alkane as oxidant and several organic solvents, the most efficient being chlorinated [62]. Ln-containing MOFs (Ln = Yb, Nd, Pr, La, Sc, Y) obtained through hydrothermal conditions were also used as catalysts, using H<sub>2</sub>O<sub>2</sub> as oxidant in CH<sub>3</sub>CN [63–65]. Rhenium was used as catalyst within the typical MeReO<sub>3</sub> complex, in presence of pyridine using H<sub>2</sub>O<sub>2</sub> as oxidant and using organic solvent [66]. The only heterogeneous process oxidizing **L** with O<sub>2</sub> as oxidant needed to use a sacrificial molecule isobutyraldehyde in dimethyl carbonate as solvent with Co/SiO<sub>2</sub> as catalyst [67]. Vanadium was used, as vanadyl arsenates using H<sub>2</sub>O<sub>2</sub> in CH<sub>3</sub>CN or TBHP in CH<sub>2</sub>Cl<sub>2</sub> [68], or as molecular complex using the VOL(OEt) (L = SAP or equivalent) using dry conditions, i.e. TBHP in alkane as oxidant and chloroform as solvent [69].

Further steps towards the use of air stable and water tolerant catalysts were achieved using species related to POMs, like (BTBA)<sub>4</sub>H [BW<sub>4</sub>O<sub>24</sub>] [70], [(C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>N]<sub>7</sub>H<sub>3</sub>[M<sub>4</sub>(H<sub>2</sub>O)<sub>2</sub>(PW<sub>9</sub>O<sub>34</sub>)<sub>2</sub>] (M = Co(II), Mn(II)) or [(C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>N]<sub>6</sub>[Fe<sup>III</sup>(H<sub>2</sub>O)<sub>2</sub>(PW<sub>9</sub>O<sub>34</sub>)<sub>2</sub>] [71], Na<sub>7</sub>PM<sub>11</sub>O<sub>39</sub> (M = Mo, W) and Na<sub>6</sub>SiW<sub>11</sub>O<sub>39</sub> [35]. With those species, H<sub>2</sub>O<sub>2</sub> as oxidants and CH<sub>3</sub>CN as solvent were used.

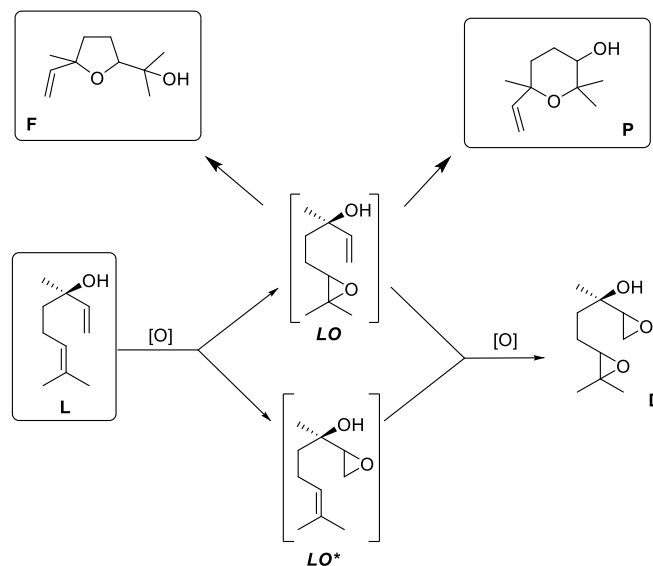
In all the references, most of oxidants used are H<sub>2</sub>O<sub>2</sub> or TBHP. Organic solvents (several chlorinated ones) are used and some air-sensitive complexes are used. Those drawbacks are the starting point of the present study.

Within the concept of Green Chemistry, developing environmentally friendly processes is very important. The work presented herein, in direct line with green chemistry requirements, uses air-stable molybdenum- or vanadium-coordination complexes [MoO<sub>2</sub>(SAP)]<sub>2</sub> (**Mo**) and [VO(SAP)]<sub>2</sub>O (**V**) as pre-catalysts (Fig. 2) for linalool oxidation with the greener oxidants H<sub>2</sub>O<sub>2</sub> and TBHP (innocuous compared to *m*-CPBA) tending to move through organic-solvent free processes. The different aspects (conversion of Linalool, selectivity towards the cyclic oxides) are discussed according to the nature of catalysts and/or oxidant. Through green metrics, the interest of those methods has been emphasized.

## 2. Results and discussion

### 2.1. Catalytic linalool oxidation – general considerations

Considering the formation of **1** and **2** from **L** through oxidation, a possible reaction pathway (Scheme 3) suggests the formation of a transient linalool epoxide (**LO**) on the most substituted olefin function [35,61]. The intramolecular OH attack of each carbon of the epoxide function of **LO** leads to corresponding cyclic derivatives 2-(5-methyl5-vinyl-tetrahydrofuran-2-yl) propan-2-ol (**1**), 2,2,6-trimethyl-6-vinyl-tetrahydro-2H-pyran-3-ol (**2**) [72] both having *cis* and *trans* derivatives, and the formation of the diepoxide of linalool (in Scheme 3) was also assessed [35].



Scheme 3. Linalool oxidation pathways inspired from Ref. [35].

### 2.2. Catalytic procedures

In the present work, the effect of the oxidant, i.e TBHP (in water or in decane) vs. H<sub>2</sub>O<sub>2</sub> (in water with/without acetonitrile) was investigated for the oxidation of **L** as well as the effect of the catalysts, [MoO<sub>2</sub>(SAP)]<sub>2</sub> (**Mo**) and [VO(SAP)]<sub>2</sub>O (**V**). The reactions were carried out for 5 h at 80 °C for TBHP or 70 °C for aqueous H<sub>2</sub>O<sub>2</sub> with several substrate/catalyst/oxidant ratios (see conditions in §1.2). The final conversion of **L** and yields of linalool oxides **1** and **2** were collected in Table 1 and kinetic studies in Figs. S1–S4. Some chromatograms were shown in Fig. S5. The formation of di-epoxide could be detected by GC-MS (see Fig. S6) but was not quantified. We focused the discussion into **L** conversion and **1** and **2** formations, without considering *cis* and *trans* features.

#### 2.2.1. Blank reactions and role of **Mo** or **V** as pre-catalysts (entries 01–04)

Blank reactions were performed with three equivalents of each oxidant but without catalyst. In each case, the yield was poor and **1** and **2** were not detected by GC. Presence of pre-catalyst **Mo** or **V** in the reaction mixture increased considerably the conversion results, showing the catalytic effect of both complexes. High **L** conversions were observed in most of the conditions with higher formation of **1** than **2** in all the cases (all entries in Fig. S3 for **Mo** and Fig. S4 for **V**). The preference of **1** over **2** is related to the stability of the 5-membered cycle vs 6-membered one. **1** is the kinetic product, formed faster than **2**. [35].

#### 2.2.2. Case of molybdenum complex **Mo**

TBHP as oxidant (Entries **Mo1–Mo6**).

With TBHP as oxidant, high **L** conversion is achieved in all cases (Fig. S1), and higher **1** and **2** yields of 49% and 28% respectively are obtained with three equivalents of TBHP in water (Entry **Mo3**) while, with the use of TBHP in decane, no significant difference of final activity is observed with different oxidant ratio three-oxidant (Entries **Mo4–Mo6**), resulting to 52–57% and 13–17% yields for **1** and **2** respectively. It has to be mentioned that TOFs are slightly lower in decane than in water, showing that fast **L** conversion is not linked to good **1** and **2** yields. The water might also react fast with the **LO** intermediate to form potential diols and thus acting negatively on the yields of target molecules.

H<sub>2</sub>O<sub>2</sub> as oxidant (Entries **Mo7–Mo12**).

With or without acetonitrile, the high **L** conversion (>94%) observed with one equivalent (Entries **Mo7 and Mo10**) and two equivalents (Entries **Mo8 and Mo11**) of oxidant diminish with three equivalents (Entries

**Table 1**

Relevant data for the oxidation of Linalool (L) and formation of corresponding **1** and **2**. Experimental conditions: Mo/Oxidant/L or V/Oxidant/L = 0.25/100X/100. T = 5 h.

Entry	Pre-Catalyst	Oxidant	X <sup>a</sup>	L conv <sup>b</sup> (%)	1 yield <sup>c</sup> (%)	2 yield <sup>d</sup> (%)	1/2 ratio	TOF <sub>max</sub> <sup>e</sup> (h <sup>-1</sup> )	TON <sup>f</sup>
O1	No	TBHP <sub>aq</sub>	3	3	0	0	–	–	–
O2		TBHP <sub>dec</sub>	3	3	0	0	–	–	–
O3		H <sub>2</sub> O <sub>2aq</sub>	3	4	0	0	–	–	–
O4		H <sub>2</sub> O <sub>2aq</sub> + ACN	3	4	0	0	–	–	–
Mo1 <sup>g</sup>	<b>Mo</b>	TBHP <sub>aq</sub>	1	90	19	8	2.37	494	328
Mo2			2	89	27	11	2.45	395	358
Mo3 <sup>h</sup>			3	99	49	28	1.75	577	382
Mo4		TBHP <sub>dec</sub>	1	94	52	13	4.00	27	370
Mo5			2	99	57	17	3.35	135	383
Mo6			3	99	55	15	3.66	482	397
Mo7		H <sub>2</sub> O <sub>2aq</sub>	1	97	15	5	3.00	1096	386
Mo8			2	99	17	6	2.83	1174	399
Mo9			3	66	23	20	1.15	110	263
Mo10		H <sub>2</sub> O <sub>2aq</sub> + ACN	1	97	51	19	2.68	1124	390
Mo11			2	98	59	25	2.36	1188	392
Mo12			3	64	32	19	1.68	158	260
V1	<b>V</b>	TBHP <sub>aq</sub>	1	72	11	6	1.83	304	289
V2			2	98	21	10	2.10	490	392
V3			3	99	24	11	2.18	1207	399
V4		TBHP <sub>dec</sub>	1	94	58	15	3.86	263	374
V5			2	98	35	8	4.37	405	393
V6			3	99	10	2	5.00	882	398
V7 <sup>h</sup>		H <sub>2</sub> O <sub>2aq</sub>	1	88	4	4	1.00	620	340
V8			2	90	6	2	1.50	665	357
V9			3	34	6	4	1.50	392	135
V10		H <sub>2</sub> O <sub>2aq</sub> + ACN	1	97	31	16	1.94	1081	386
V11			2	99	34	19	1.79	1177	392
V12			3	98	32	29	1.10	175	390

<sup>a</sup> X = equivalents of oxidant.

<sup>b</sup> L conversion = n(L) consumed at (5 h)/n(L) engaged (in %).

<sup>c</sup> 1 yield = n(**1**) formed at 5 h/n(L) engaged (in %) (calculated from GC).

<sup>d</sup> 2 yield = n(**2**) formed at 5 h/n(L) engaged (in %).

<sup>e</sup> TOF<sub>max</sub> = n(L) transformed/n(catalyst)/0.33 at 20 min (in h<sup>-1</sup>).

<sup>f</sup> TON = n(L) transformed/n(catalyst) at 5 h.

<sup>g</sup> Mo/L molar ratio = 0.27%.

<sup>h</sup> Mo/L or V/L molar ratio = 0.26%.

Mo9 and Mo12) with a conversion around 65%. This could be due to substrate overoxidation or catalyst destruction/inhibition.

The role of solvent is positive for **1** and **2** yields, obtaining 32–59% **1** yield and 19–25% **2** yield with acetonitrile vs. 15–23% **1** yield and 5–20% **2** yield without acetonitrile. Acetonitrile seems to prevent side reactions like the water attack on transient LO. As it is seen, pre-catalyst activation is not affected by the presence/absence of solvent (but **1** and **2** yields) and the role of oxidant ratio is detrimental. Indeed, **L** is very fast consumed with one and two equivalents (TOF around 1100 h<sup>-1</sup>, see Fig. S3, Mo7, Mo8, Mo10, Mo11) and slowly consumed with three equivalents (TOF value of 110–150 h<sup>-1</sup> as seen in Fig. S3 Mo9, Mo12). As observed with TBHP, low **L** conversions (Fig. S3 Mo7–Mo9) with constant increasing formation of **1** and **2** can be a sign of partial destruction/inhibition of the catalyst.

### 2.2.3. Case of vanadium complex V

2.2.3.1. TBHP as oxidant (entries V1–V6). With TBHP as oxidant, catalyst **V** gave final **L** conversions >94% for entries V2–V6. In the case of entry V1, conversion falls down to 72%. The highest **1** and **2** yields were obtained with one equivalent of TBHP<sub>dec</sub> with 58% and 15% respectively (entry V4 and Fig. S4). Different activity is observed according to the nature of the solvent used with TBHP. Indeed, in entries V4–V6 with TBHP<sub>dec</sub>, increasing quantity of oxidant decreases **1** and **2** yields. A reverse observation can be done in the case of entries V1–V3 with TBHP<sub>aq</sub>, **1** and **2** yields increasing with higher oxidant ratio. According to TOF values, catalyst **V** seems to be faster activated in the case of water than in the case of decane. The apolar vs polar nature of solvent can be a reason of this activity difference. The highest TOF, achieved in

V3 with TBHP<sub>aq</sub> (1207 h<sup>-1</sup>), leads to the highest **1** and **2** yields among V1–V3 entries (see Fig. S4). In the contrary, fastest reaction with highest TOF with TBHP<sub>dec</sub> (882 h<sup>-1</sup>) gave the lowest **1** and **2** yields (Entry V6). This observation leads to the same conclusion than for catalyst **Mo** according to the reverse relationship between activity and selectivity in apolar medium for catalyst **V**. One side reaction is certainly faster than cyclisation with three equivalents of TBHP. The absence of water could be the reason.

2.2.3.2. H<sub>2</sub>O<sub>2</sub> as oxidant (entries B7–B12). High conversions were obtained in case of one and two equivalents of oxidant (Entries V7–V8) without acetonitrile, with a significant decrease (34%) with three equivalents (Entry V9). This could be related to the low ability of H<sub>2</sub>O<sub>2</sub> to mix with the organic phase, decreasing the contact between catalyst and the reagent, lowering the activity of the catalyst [10] as well as **1** and **2** yields (2–6%) although water presence seemed to favour cyclisation. This assumption was verified after addition of acetonitrile, since very high **L** conversions were obtained (Entries V10–V12), giving relatively good **1** (31–34%) and **2** (16–29%) yields, although lower than with **Mo**. Faster performance of the catalyst **V** is observed after addition of acetonitrile (Entries V10–V11) with very high TOF values of 1081 h<sup>-1</sup> and 1177 h<sup>-1</sup> respectively, reaching completion in the case of entry V11 after 20 min (Fig. S1-b2). This is not the case when three equivalents of oxidant are added (Entry V12) since a slow activity is observed (TOF of 175 h<sup>-1</sup>) certainly indicating that the use of excess of hydrogen peroxide affected the performance of the catalyst, maybe transforming it into inactive species. This feature is seen in the complete kinetic study (Fig. S1 – b3) where a plateau is observed after 20 min of reaction.

### 2.3. About mass balance considerations

The nature of the reaction mixture, defined here by the “mass balance”, can give us another proof of efficiency of a process. This value corresponds to the molar ratio of all the identified species in the reaction through GC-FID analyses – i.e. remaining **L** and formed **1** and **2** at the time of the sample - on the starting number of moles of **L**.

$$\text{mass balance (in \%)} = \frac{(n_L + n_1 + n_2)_{t=5h}}{(n_L)_{t=0}}$$

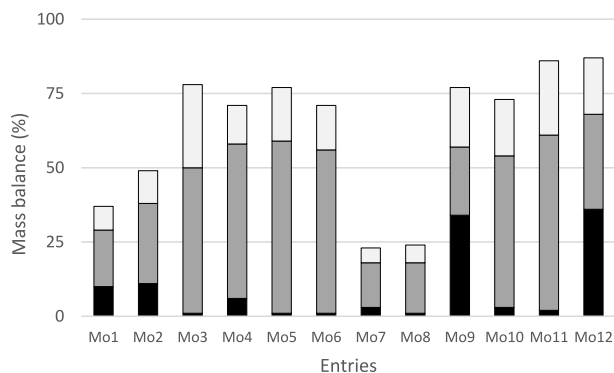
Thus, the highest mass balance is good for a reaction when few side-products remain unidentified. From an industrial point of view, the selectivity of reaction is an important parameter, indication of a good process, no matter the kinetic of the reaction. But to be completely interesting, a chemical process needs to gather good conversion (minimal  $n_L$  at 5 h) and good yields into the expected products ( $n_1 + n_2$  being close to the starting  $n_L$ ).

#### 2.3.1. Case of molybdenum complex Mo

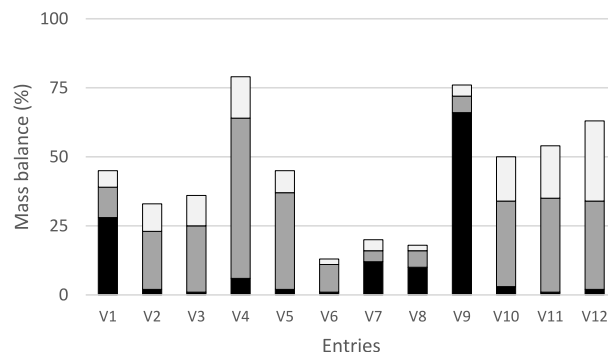
The values of mass balance at the end of the reaction with complex **Mo** (Scheme 4) were high in most of the cases (>70%), showing a relative high selectivity in several processes except in when water was present and one or two equivalents of oxidant used (entries *Mo1*, *Mo2*, *Mo7* and *Mo8*). This can be a beginning of mechanistic explanation; **L** conversion was high but relatively low **1** and **2** yields indicating another reactivity of the **LO** intermediate than cyclisation. In the reaction, non-identified/quantified species are certainly the reason of mass balance fall in the case of  $H_2O_2$  as oxidant. Thus, **L** might be transformed into a species like the bis-epoxide **D** that could be detected but not quantified.

#### 2.3.2. Case of vanadium complex V

Mass balance values at the end of the reaction (Scheme 5) were low (<45%) in the case of  $TBHP_{aq}$  (Entries *V1*–*V3*), which is the same in case of  $H_2O_{2aq}$  (Entries *V7*–*V8*) except when three equivalents of oxidant are used (Entry *V9*), but this is an artefact due to the high amount of remaining linalool (low conversion), **1** and **2** yield being comparable to those from entries *V7* and *V8*. In case of  $TBHP_{aq}$  and  $H_2O_2$  in acetonitrile, catalyst **V** gave high mass balance values ( $\geq 45\%$ ) (Entries *V4*, *V5* and *V10*–*V12*). Results from Entry *V6* differ (<20%) since it seems that the number of unidentified products is high. Those species could be the bis epoxide but also could correspond - due to high oxidant ratio and thus more water - to the reaction between water and epoxide. Thus, the conclusion is that the nature and the ratio of the oxidant is important to start the reaction, presence of water playing a non-negligible role for both aspects of the reaction, i.e. inhibiting/destroying the catalyst and/or reacting with the epoxides.



**Scheme 4.** – Mass balance (%) in the case of Entries *Mo1*–*Mo12* (from Table 1). Remaining **L** (black), **1** yield (dark grey), **2** Yield (pale grey).



**Scheme 5.** – Mass balance in the case of Entries *B* (from Table 1). Remaining **L** (black), **1** yield (dark grey), **2** Yield (pale grey).

### 2.4. Green metrics considerations

Considering the variety of oxidants tested, it was interesting to consider the green metrics for such reactions. Following the simple rules edited by Andraos on Green metrics, [73] we considered all solvents (water, acetonitrile and decane) as waste. All parameters defined in this article have been explained in details in SI. Results for each entry in presence of complexes **Mo** and **V** are presented in radial mode in Scheme 6 and numerical data are gathered in Table S2.

Both complexes **Mo** and **V** have shown efficient **L** oxidation in absence of organic solvent using greener oxidant in aqueous medium. **1** and **2** yields are clearly influenced by the presence of solvent. Full conversion, and high yields can be obtained in absolute solvent-free conditions, but enhancing the selectivity towards the targeted products requires further improvements.

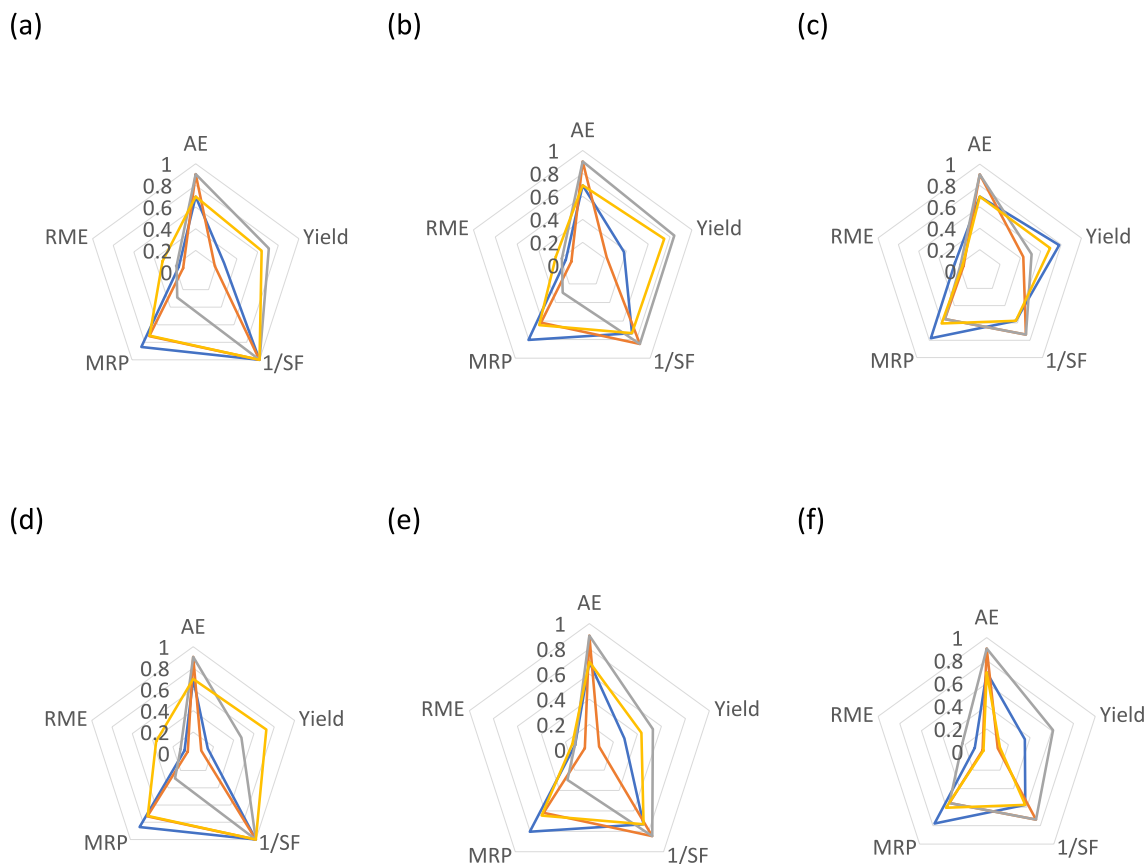
Several oxidants conditions and different catalysts are interesting factors to be discussed in in order to assess an efficient green process. Indeed, the different conditions on nature of oxidant influence **1** and **2** formation, considering that some cases used organic solvent and that the catalysts were not recovered.

Thus, Atom Efficiency (AE) changes with the nature of oxidant.  $H_2O_2$  giving better AE than  $TBHP$  due to the molar mass of the oxidant with 0.90 for  $H_2O_2$  vs. 0.70 for  $TBHP$  since the by-product is  $H_2O$  vs  $tBuOH$ . Stoichiometric factor (SF) is ideal with one equivalent of oxidant and lower with higher ratio being 0.73 (resp. 0.85) and 0.58 (resp. 0.73) with two and three equivalents of  $TBHP$  (resp.  $H_2O_2$ ). The Reaction Mass efficiency (RME) is very low, 0.03 for entry *V6* until 0.36 for *V4*, being obviously better with lower oxidant ratio since most of reagents introduced react and nothing is wasted. The Mass Recovery Parameter (MRP) in each reaction is better with the use of  $TBHP$  in water because this oxidant is in higher concentration in water and thus, there is less non-useful matter within the reaction batch. Yields (addition of **1** and **2** yields) are better with the use of  $H_2O_2$  with acetonitrile. Those results represent a proof of a concept of a cleaner process in which low oxidant ratio and no organic solvent can lead to a reaction with high recovery and low waste.

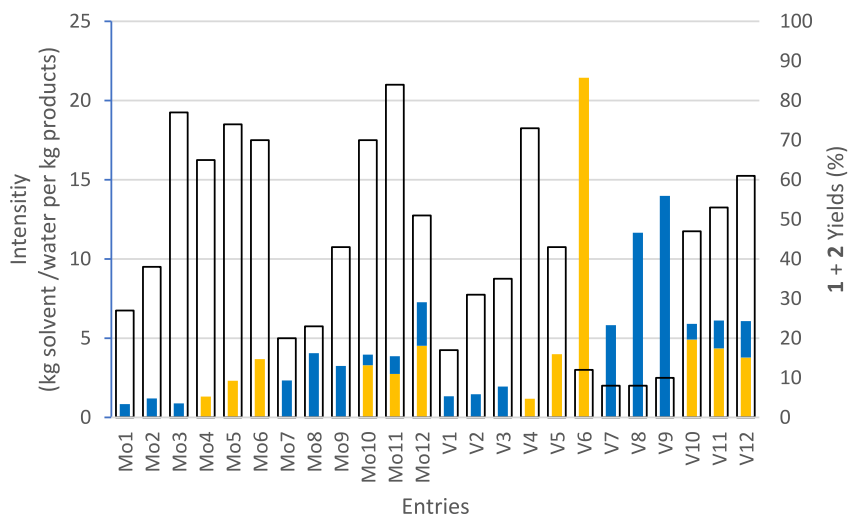
In the optic of finding an efficient process under organic-solvent-free process, we considered two other green metrics considering the role of solvent and water, with the Solvent Intensity (SI) and Water Intensity (WI) parameters. Those parameters indicate the mass of all organic solvent or water used in a process over the mass of product. [74] The smaller is the value, the less quantity of water is used per quantity of product.

The results have been indicated considering all entries using metal complexes in Scheme 7 and data are present in Table S2.

It is very interesting to see that some 8/12 entries are extremely efficient (**1** + **2** yield superior to 60%). Among those processes, one (*Mo3*) used a solvent-free process but using three equivalents of  $TBHP$ .



**Scheme 6.** Radial distribution with Green metrics for all processes. Numerical Data are in SI. The Radial graphs a, b and-c (resp. d, e and f) correspond to complex **Mo** (resp. **V**) with one, two and three equivalents of oxidants. Yield correspond to the sum of **1** and **2** yields. The different oxidants have been depicted as followed. The colors are upon the oxidants. TBHP in water (blue), TBHP in decane (yellow), H<sub>2</sub>O<sub>2</sub> in water (orange) and H<sub>2</sub>O<sub>2</sub> in water plus acetonitrile (grey).



**Scheme 7.** – Solvent Intensity (yellow bars) and Water intensity (blue bars) for all conditions from Table 1. Axis for the intensities is Left axis. Sum of the yields (in %, Right axis white bars) (c). Numerical data are in Table S2 for Intensities and Table 1 for Yields.

Despite this high amount of oxidant, the water intensity value is not so high. Processes with TBHP in decane (*Mo4-6*, and *V4*) are efficient but should be avoided due to the nature of organic solvent. Finally, H<sub>2</sub>O<sub>2</sub> with acetonitrile (*in Mo11-12 and V12*), a very spread method according to literature gave Solvent and Water intensities not in agreement with a greener process.

Finally, in order to compare those results with the literature data collected in Table S1, we selected all data with relative similar conditions, i.e. using metal-catalysts with equivalent metal ratio, a reaction time not exceeding 8 h and **1 + 2** yields superior to 60%. Six conditions were found. Most of the experiments used molecular catalysts and H<sub>2</sub>O<sub>2</sub> as oxidant. Most were POM types. All needed organic solvent as chloroform and acetonitrile.

Since both solvents must be banned from the list of greener processes, the entry *Mo3* is the first organic solvent-free process with relatively good capacity observed until now with 87% yield of **1 + 2** after 5 h of reaction with 0.5 mol% metal/substrate only.

### 3. Conclusion

Molybdenum and vanadium coordination complexes [MoO<sub>2</sub>(SAP)]<sub>2</sub> and [VO(SAP)]<sub>2</sub>O were tested as pre-catalysts for the oxidation of a biomass-issued tertiary alcohol, linalool, in the presence of environmentally benign oxidants TBHP (in water or decane) and H<sub>2</sub>O<sub>2(aq)</sub> (with or without acetonitrile). Attractive aspects in straight line of Green Chemistry principles, i.e. greener oxidants, easy synthesis of active catalysts, organic solvent-free catalytic protocols and bio-sourced substrates were tested. Efficient conversion of linalool gave selectively two valuable compounds, important intermediates in chiral synthesis. As seen by the green metrics considerations, better or equivalent yields could be obtained with the use of solvent but this is detrimental to Green Chemistry requirements. For the first time, we described an organic solvent-free process for such transformation. Theoretical studies to complete a plausible mechanism in the case of both complexes are under progress.

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### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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### Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.tgchem.2023.100029>.

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