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Lewis acid-catalyzed oxidative rearrangement of tertiary allylic alcohols mediated by TEMPO

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ABSTRACT

Two methods for the oxidative rearrangement of tertiary allylic alcohols have been developed. Most of tertiary allylic alcohols studied were oxidized to their corresponding transposed carbonyl derivatives in excellent to fair yields by reaction with TEMPO in combination with PhIO and $Bi(OTf)_3$ or copper (II) chloride in the presence or not of oxygen. Other primary oxidants of TEMPO such as $PhI(OAc)_2$, *m*CPBA, and Oxone® were unsatisfactory giving the enone in modest to low yields.

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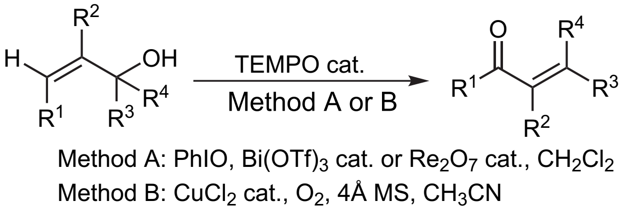
1. Introduction

β,β′-Difunctionalized enones are essential and versatile intermediates in organic synthesis.[1] Moreover, this motif is frequently encountered in a variety of biologically active natural products.[2] One of the most used strategy for the preparation of this class of compounds is a two-step alkylative 1,3-carbonyl transposition of α,β-unsaturated ketones, which entails a 1,2-addition of organometallic reagents followed by an oxidative rearrangement of the resulting tertiary allylic alcohols. Until recently, the oxidative transposition step was exclusively effected by using oxochromium (VI)-based reagents such as CrO_3 and mostly its less acidic derivatives, PCC and PDC.[3,4] However, if this oxidation method has been used in a large number of syntheses,[5] for some substrates the yield of rearrangement was low either because of a very slow oxidation reaction[5h] or of the formation of by-products such as epoxides[5m] or fragmentation products.[3b,6] Safety hazards associated with these oxidants and their toxic by-products have urged organic chemists to develop eco-friendly strategies for this oxidative rearrangement. In 2004, Iwabuchi and co-workers have reported the use of excess of IBX in DMSO to produce substituted cycloalkenones from cyclic tertiary allylic alcohols.[7] The same author described two more general method than IBX employing as oxidants either stoichiometric amount of oxoammonium salts or TEMPO and $NaIO_4$ as a co-oxidant.[8] Very recently, Ishihara and co-workers developed a 2-iodoxybenzenesulfonic acid-promoted oxidative rearrangement of tertiary allylic alcohols with Oxone® at 60 °C.[9]

In relation with an ongoing project aimed to explore the use of TEMPO/co-oxidants in organic synthesis,[10] we have recently reported in preliminary accounts two protocols for the oxidative rearrangement of tertiary allylic alcohols using TEMPO in the presence of PhIO or copper(II) salts as primary oxidants (Scheme 1).[11] We now reported in full details, studies of these methods of oxidative rearrangement of tertiary allylic alcohols as well as with other TEMPO/co-oxidant systems.



Method A: PhIO, $Bi(OTf)_3$ cat. or Re_2O_7 cat., CH_2Cl_2
Method B: $CuCl_2$ cat., O_2, 4Å MS, CH_3CN

Scheme 1.

2. Results and discussion

2.1. Oxidative rearrangement with the TEMPO/PhIO/Lewis acid system

We started studying the oxidative rearrangement of 1-*n*-butyl-2-cyclohexen-1-ol **1a**, a representative tertiary allylic alcohol substrate, with TEMPO/PhIO/$Yb(OTf)_3$, a system we recently reported

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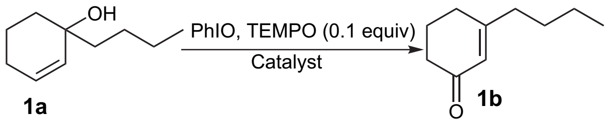
its ability to oxidize readily and chemoselectively alcohols to carbonyl compounds. In the presence of a catalytic amount of TEMPO and $Yb(OTf)_3$ and PhIO (1.3 equiv), compound **1a** afforded the unsaturated ketone **1b** in only 40% (Table 1, entry 1). We therefore screened the catalytic activity of a range of protic or Lewis acids on the oxidation of **1a**. Among metal triflates tested, $Bi(OTf)_3$ appeared to be the most efficient to promote the oxidative rearrangement of **1a** affording the enone **1b** in 77% (entry 4).[12] The presence of 4 Å molecular sieves in the reaction medium reduced the amount of side products improving the yield (entry 5).[13] Disappointingly, strong acids such as *p*-toluenesulfonic acid had a weak catalytic activity on the oxidative rearrangement providing **1b** in 64% yield (entry 6). We finally tested Re_2O_7 as a catalyst because, in addition to its Lewis acid character,[14] it is known to induce a 1,3-isomerization of allylic alcohols,[15,16] the very likely first step of the oxidative rearrangement mediated by TEMPO/PhIO/Lewis acid.[11a] Unfortunately, relatively high loading of Re_2O_7 was necessary for the transposition to occur and the desired enone **1a** was obtained in a modest yield (entry 7).

Table 1
Study of the oxidative rearrangement of 1-butyl-2-cyclohexen-1-ol **1a** with PhIO/TEMPO system in the presence of various Lewis or protic acids

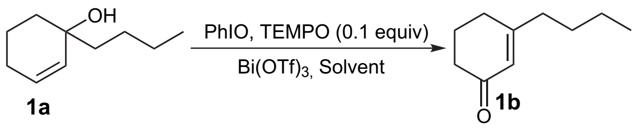


Entry	Catalyst (mol %)	Solvent	Temp (°C)	Time (%)	Yield[a] (%)
1	$Yb(OTf)_3$ (10)	CH_2Cl_2	20	1	40
2	$Sc(OTf)_3$ (20)	CH_2Cl_2	0	0.5	41
3	$Zn(OTf)_3$ (30)	CH_2Cl_2	20	1	30
4	$Bi(OTf)_3$ (8)	CH_2Cl_2	0	1	77
5	$Bi(OTf)_3$ (8)[b]	CH_2Cl_2	0	0.5	84
6	*p*-TsOH(40)	CH_2Cl_2	20	1	64
7	Re_2O_7 (15)	CH_2Cl_2	0	1	44

[a] Isolated yield.
[b] 4 Å MS was added (0.08 g/mmol).

We next examined solvent effects on the TEMPO/PhIO/$Bi(OTf)_3$-catalyzed oxidative transposition on compound **1a**. As seen in Table 2, all solvents tested were less efficient than dichloromethane in terms of yields and catalytic activity. Addition of water to dichloromethane significantly lowered the reaction rate and the yield by increasing the amount of by-products (entry 6). Much higher solubility of $Bi(OTf)_3$ in water than in dichloromethane might explain the decrease of the oxidative rearrangement rate by lowering the concentration of the catalyst in the organic phase.[17]

Table 2
Solvent dependence of $Bi(OTf)_3$- promoted the oxidative rearrangement of **1a** with PhIO/TEMPO system



Entry	Solvent	$Bi(OTf)_3$ (mol %)	Time (min)	Yield (%)
1	THF	50	60[a]	41
2	Toluene	25	30[a]	58
3	CH_3CO_2Et	25	30[b]	63
4	CH_3NO_2	8	15[b]	56
5	CH_3CN	15	30[a]	62
6	CH_2Cl_2–H_2O	20	120[b]	35

[a] 0 °C.
[b] Room temperature.

Having optimized the reaction conditions, we tested the scope of this process on a range of substrates and the results are outlined in Table 3. Transposed cyclohexenones **1a**–**4a** were obtained in good to fair yields (entries 1–4). Crowded 4,4-disubstituted cyclohexenol **5a** was slowly oxidized and required high loading of catalyst, highlighting the extreme sensitivity of the TEMPO-based oxidation method to the environment of the carbinol moiety (entry 5).[18] In contrast to the oxidative rearrangement with oxychromium(VI)-reagents, diastereomeric mixture of carveol reacted sluggishly in the presence of TEMPO/PhIO system to afford 3-methylcarvone in only 19% yield accompanied by several byproducts (entry 6).[19] Five-membered substrates readily responded to the TEMPO-based oxidative rearrangement to provide enones **7a**–**9a** in good yields (entries 7–9). 12-Macrocyclic compound **10a** exhibit low reactivity furnishing, after 24 h, the desired enone in only 35% yield (based on recovered starting material). Iwabuchi and co-workers have already pointed out that medium and macrocyclic tertiary allylic alcohols reacted much more slowly using TEMPO/$NaIO_4$ system than their corresponding five-and six-membered derivatives.[7b] We next aimed to extend the scope of our method to the more challenging acyclic substrates. Indeed, these compounds are known to be reluctant to undergo 1,3-oxidative rearrangement and also to give fragmentation products.[3a,b,6a,5e] Treatment of compound **11a** with PhIO/TEMPO/$Bi(OTf)_3$ or Re_2O_7 gave a mixture of products in which the desired enone was not detected (entry 11). Another interesting extension of this oxidation is that of tertiary vinyl carbinols, which furnishes α,β-unsaturated aldehydes.[3b] Conversely to $Bi(OTf)_3$, Re_2O_7 efficiently catalyzed the oxidative rearrangement of vinyl alcohol **12a** to give **12b** in fair yield (entry 12). Under the same reaction conditions, cyclohexanol derivative **13a** gave cyclohexylideneacetaldehyde **13b** in only modest yield (entry 13).

2.2. Aerobic-oxidative rearrangement with Cu(II) salts/TEMPO

Even if the oxidative rearrangement with TEMPO/PhIO/$Bi(OTf)_3$ or Re_2O_7 system gave satisfactory results on most substrates, being competitive with the other existing methods, this process was not applicable to acyclic tertiary allylic alcohols. For this reason and in order to find a more simple procedure, we surveyed the literature to find a cheap and commercially available reoxidant of TEMPO, which can also act as a Lewis acid, necessary for the first step of the oxidative rearrangement: the allylic rearrangement of tertiary allylic alcohols via an allylic cation.[11a] Because copper(II) salts were used in many instances as primary oxidants of TEMPO and also are mild Lewis acids,[20] we thought that the couple TEMPO/Cu(II) could promote the oxidative rearrangement of tertiary allylic alcohols. The first experiment was quite disappointing since, in the presence of TEMPO and $CuCl_2.2H_2O$ (3 equiv), 1-butylcyclohex-2-en-1-ol **1a** led to the transposed enone **1b** in 31% yield (Table 4, entry 1).

The enone yield was greatly improved by addition of 4 Å molecular sieves, which traps HCl formed during the oxidation reducing strongly the formation of dehydration products (entry 2). $Cu(NO_3)_2$ and $Cu(ClO_4)_2$ gave similar results than $CuCl_2$ whereas $CuBr_2$ afforded almost exclusively decomposition products (entries 3–5). With other salts such as $CoCl_2$ and $Mn(NO_3)_2$, the conversion was very slow, giving mainly the corresponding 1,3-transposed allylic alcohol of **1a** and dehydration compounds.[21]

Semmelhack and co-workers have shown that, in the presence of oxygen, copper salts could be used catalytically for the TEMPO-mediated oxidation of alcohols.[20a] In the optimized conditions, copper-catalyzed aerobic oxidative rearrangement of tertiary allylic alcohol **1a** provided the enone **1b** in 90% yield (entry 7).

We then tested the scope of this process on a variety of tertiary allylic alcohols. As seen in Table 5, diversely substituted six-membered substrates were smoothly converted in good to excellent

Table 3

$Bi(OTf)_3$- or Re_2O_7-catalyzed oxidative rearrangement of tertiary allylic alcohols with TEMPO in combination with PhIO

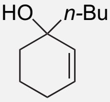
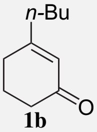
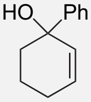
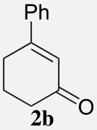
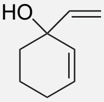
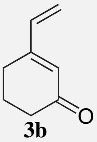
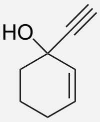
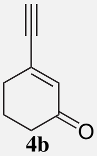
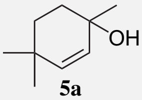
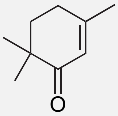
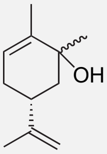
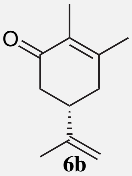
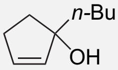
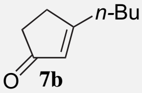
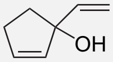
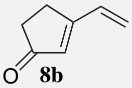
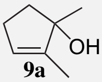
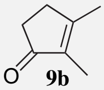
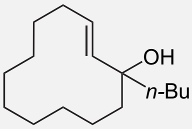
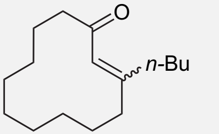
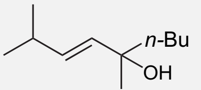
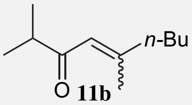
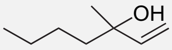
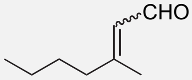
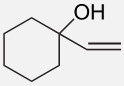
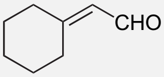
Entry	Substrate	Method[a]	Time (h)	Temperature (°C)	Product	Yield[b] (%)
1	 **1a**	A	1	0	 **1b**	84
2	 **2a**	A	1	0	 **2b**	73
3	 **3a**	A	1	0	 **3b**	72
4	 **4a**	A[c]	16	20	 **4b**	67
5	 **5a**	A[c]	5	20	 **5b**	60
6	 **6a**	A[c]	1	20	 **6b**	19
7	 **7a**	A	1	0	 **7b**	80
8	 **8a**	A	0.5	0	 **8b**	78
9	 **9a**	A	0.5	0	 **9b**	78
10	 **10a**	A[c]	24	20	 **10b**	22[d]
11	 **11a**	A, B	16	0	 **11b**	-[e]

Table 3 (*continued*)

Entry	Substrate	Method[a]	Time (h)	Temperature (°C)	Product	Yield[b] (%)
12	 **12a**	B	1	20	 **12b**	58
13	 **13a**	B	1	20	 **13b**	40

[a] General conditions: PhIO (1.2 equiv), TEMPO (0.1 equiv), catalyst. For method A: $Bi(OTf)_3$ (8 mol %) and 4 Å MS (0.08 g/mmol); method B: Re_2O_7 (20 mol %) and 4 Å MS (0.13 g/mmol).

[b] Isolated yield.

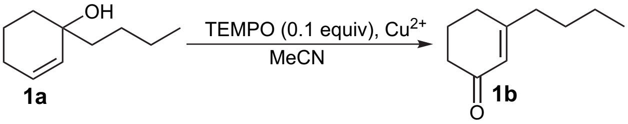
[c] 25 mol % of $Bi(OTf)_3$ were added.

[d] 37% of the starting material were recovered.

[e] A mixture of unidentified products was obtained.

Table 4

Influence of the copper (II) salt on the oxidative rearrangement of tertiary allylic alcohol **1a** mediated by TEMPO



Entry	Cu^{2+} salt	Equiv	4 Å MS (g/mmol)	Temp (°C)	Time (h)	Yield[a] (%)
1	$CuCl_2$	3	—	rt.	0.5	31[b]
2	$CuCl_2$	3	0.23	rt.	1	78
3	$Cu(NO_3)_2$	3	0.23	rt.	1	83
4	$Cu(ClO_4)_2$	3	0.23	rt.	1	81
5	$CuBr_2$	3	0.23	0	1	30
6	$CuCl_2$	0.2	0.15	rt.	72	58[c,d]
7	$CuCl_2$	0.5	0.15	rt.	7	90[c]

[a] Isolated yield.

[b] Formation of elimination products.

[c] Under O_2 (balloon).

[d] 29% of the starting material were recovered.

yields to their corresponding transposed enones (entries 1–7). However, sterically crowded substrates such as **6a** and **14a** required a high loading of $CuCl_2$ to be oxidized at a reasonable rate (entries 6 and 7). It is noticeable than 2-methylcarveol **5a** was converted to 3-methylcarvone in high yield as contrasted with that obtained using TEMPO/PhIO system (89% versus 19% yield) (entry 5). Aerobic copper oxidation of five-membered substrates proceeded readily to afford β-substituted cyclopentenones in fair yields (entries 8 and 9). In the presence of 2 equiv of $CuCl_2$, medium and macrocyclic substrates furnished the expected products in high yields (entries 10 and 11). In contrast to the method using PhIO as a bulk oxidant (Table 3, entry 11), TEMPO/$CuCl_2$ effected the oxidative rearrangement of acyclic compound **11a** in a satisfactory yield (entry 12). TEMPO/$CuCl_2$ system was less effective for the oxidative rearrangement of tertiary vinyl carbinols than that of TEMPO/PhIO/Re_2O_7 (compare Table 3, entry 12 and Table 5, entry 13).

2.3. Study of the oxidative rearrangement with other cooxidants of TEMPO

We first tested TEMPO/$PhI(OAc)_2$ system, which is becoming one of the most used method for the oxidation of alcohols in organic synthesis (Table 6).[22] This oxidizing system led the allylic alcohol **1a** unchanged after 24 h at room temperature (entry 1). We next screened several acids and, in all cases, a mixture of the desired enone **1b** and of the allylic acetate **1c** was obtained in good yields (entries 2 and 4). Evidently, the mechanism of formation of secondary allylic acetate involve a solvolysis of the tertiary alcohol to an allylic carbonium ion which collapses with acetic acid at the lesser substituted termini to generate **1c**. In the conditions developed by Rychnovsky and Vaidyanathan: MCPBA, TEMPO and Bu_4NBr catalytic, the epoxide **1d** was obtained as a sole product (Table 6, entry 1).[23] In contrast, in the presence of $Bi(OTf)_3$, the allylic rearrangement occurred affording the desired enone albeit in low yield accompanied by a mixture of epoxides **1d** and **1e** (entry 2). Lastly, in the presence of TEMPO, Oxone® and tetrabutylammonium bromide compound **1a** gave a mixture of products, among them the desired enone **1b** was isolated in less than 10% yield.[24]

3. Conclusion

In conclusion, we have successfully developed two mild and environmentally friendly methods for Lewis acid catalyzed-oxidative rearrangement of tertiary allylic alcohols to β-disubstituted enones. The advantages of TEMPO/$CuCl_2$/O_2 system over TEMPO/PhIO/$Bi(OTf)_3$ or Re_2O_7 system are the availability of its reagents and their costs and it gives better results for substituted six-membered cyclic, macrocyclic and acyclic allylic tertiary alcohols. Unsaturated aldehydes are more readily obtained and with a better yields from tertiary vinyl carbinols with TEMPO/PhIO oxidizing process.

4. Experimental section

4.1. General procedures

^1H NMR spectra were recorded in $CDCl_3$ (δ_H=7.25) at ambient probe temperature on a Bruker AC 200 (200 MHz) spectrometer.

Table 5
Copper(II) chloride-catalyzed oxidative rearrangement of tertiary allylic alcohols mediated by TEMPO

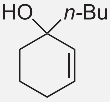
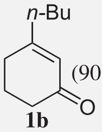
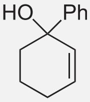
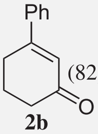
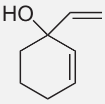
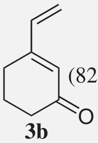
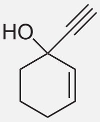
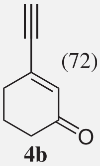
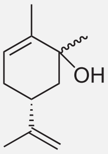
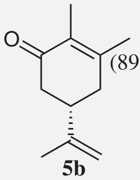
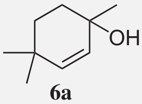
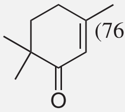
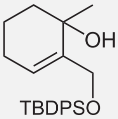
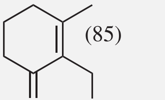
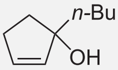
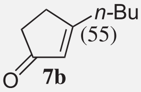
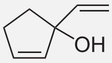
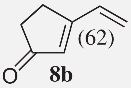
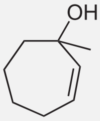
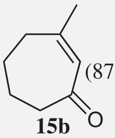
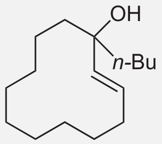
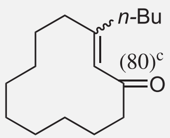
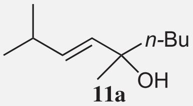
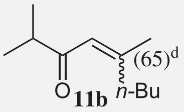
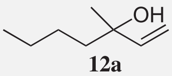
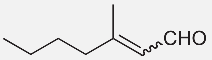
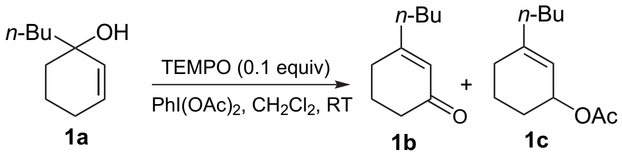
Entry	Substrate	Method[a]	Time (h)	Product[b] (yield %)
1	 **1a**	A	7	 **1b** (90)
2	 **2a**	A	5	 **2b** (82)
3	 **3a**	A	6	 **3b** (82)
4	 **4a**	B	8	 **4b** (72)
5	 **5a**	B	48	 **5b** (89)
6	 **6a**	B	6	 **6b** (76)
7	 **14a**	B	10	 **14b** (85)
8	 **7a**	A	7	 **7b** (55)
9	 **8a**	A	7	 **8b** (62)
10	 **15a**	A	48	 **15b** (87)

Table 5 (*continued*)

Entry	Substrate	Method[a]	Time (h)	Product[b] (yield %)
11	 **10a**	B	48	 (80)[c] **10b**
12	 **11a**	B	48	 (65)[d] **11b**
13	 **12a**	B	30	 **12b** (45)[c]

[a] Method A: TEMPO (0.1 equiv), $CuCl_2·2H_2O$ (0.5 equiv), O_2 (balloon), 4 Å MS, rt; Method B: TEMPO (0.1 equiv), $CuCl_2·2H_2O$ (2 equiv), 4 Å MS, rt.
[b] Isolated yield.
[c] Ratio *E*/*Z*=1.8/1.
[d] Ratio *E*/*Z*=2.5/1.

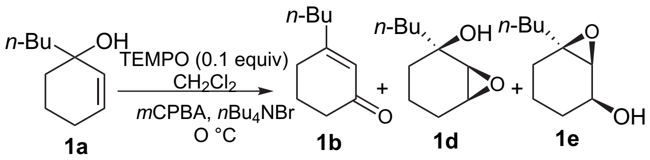
Table 6
Oxidative rearrangement of **1a** with TEMPO/$PhI(OAc)_2$



Entry	Catalyst (mol %)	Time (h)	**1b** (%)	**1c** (%)
1	—	24[a]	—	—
2	$Bi(OTf)_3$ (4)	0.75	41	32
3	$Sc(OTf)_3$ (5)	1	37	30
4	*p*-TSA (20)	1	51	24

[a] No reaction occurred.

Table 7
Study of the reaction between **1a** and TEMPO/*m*CPBA/*n*Bu_4NBr



Entry	Catalyst (mol %)	Time	**1b** (%)	**1d** (%)	**1e** (%)
1	—	2	0	88	0
2	$Bi(OTf)_3$	1	9	22	28

Data are presented as follows: chemical shift (in ppm on the δ scale relative to $\delta_{TMS}=0$), multiplicity (s=singlet, d=doublet, t=triplet, q=quadruplet, m=multiplet, br=broad), integration, coupling constant and interpretation. ^{13}C NMR spectra were recorded at ambient probe temperature on a Bruker AC 200 (50.3 MHz) in $CDCl_3$ used as reference ($\delta_C=77.0$). High resolution mass spectrometry (HRMS) analyses were conducted using a Thermofinigan-MAT 95 XL instrument. IR spectra were recorded on a Perkin-Elmer 298 spectrophotometer. Optical rotations were measured on a Perkin-Elmer 141 polarimeter at the sodium D line (598 nm). Melting points were determined on a Büchi 530 apparatus and are uncorrected. Reagents and solvents were purified by standard means. Tetrahydrofuran was distilled from sodium wire/benzophenone and stored under a nitrogen atmosphere. Acetonitrile, dichloromethane, dimethylformamide were distilled from calcium hydride. Powdered 4 Å molecular sieves (Aldrich) was dried at 150 °C during 6 h. All other chemicals were used as received. $Bi(OTf)_3$ was obtained from Alfa. Tertiary alcohols **1a**[7a], **2a**[7a], **3a**[25], **4a**[26], **5a**[3b], **6a**[18], **7a**[27], **8a**[6b], **9a**[28], **11a**[7a], **12a**[29], **13a**[30], **14a**[31], **15a**[32] were prepared following the literature procedures. PhIO was obtained according to the reported procedure.[33]

4.2. (*E*)-1-*n*-Butyl-2-cyclododecen-1-ol (10a)

To a cooled solution (−78 °C) of (*E*)-2-cyclododecen-1-one[34] (0.52 g, 2.9 mmol) in THF (10 mL) were added dropwise *n*-BuLi

(2.5 M in hexanes, 1.7 equiv). The reaction was warmed up to −30 °C, stirred at this temperature for 1 h and ethanol was added. After stirring 5 min at this temperature, ether and saturated NH_4Cl solution were added. The aqueous phase was extracted once with ether and the combined extracts were dried (Na_2SO_4) and concentrated under reduced pressure. The resulting oil was purified by chromatography on silica gel (ether–petroleum ether, 1/9) to give **10a** as an oil (0.39 g, 57% yield). IR (film): 3447 cm^{-1}. ^1H NMR (C_6D_6): 0.9 (t, 3H, J=6.2 Hz, Me), 1.12–1.6 (m, 23H), 2.12–2.16 (m, 2H), 5.24 (d, 1H, J=15.6 Hz), 5.46 (ddd, 1H, J=5.1, 9.8, 15.6 Hz). ^{13}C NMR: 14.4, 21.8, 23.7, 24.5, 24.8, 25.0, 25.1, 26.0, 26.2, 26.9, 31.2, 40.1, 42.3, 75.5, 128.2, 137.5. HRMS: calcd for $C_{16}H_{30}O$ (M^+) 238.2297; found: 238.2295.

4.3. General procedure for the oxidative rearrangement of tertiary alcohols

4.3.1. With TEMPO/PhIO/Bi(OTf)₃ or Re₂O₇. To a solution of tertiary alcohol (1 mmol) in CH_2Cl_2 (5 mL) were added PhIO (0.264 g, 1.2 equiv), TEMPO (15.6 mg, 0.1 equiv) and 4 Å molecular sieves (0.08 and 0.13 g/mmol with $Bi(OTf)_3$ and Re_2O_7, respectively). The suspension was cooled to 0 °C and Lewis acid was added. When high loading of $Bi(OTf)_3$ (25 mol %) was used (Table 3, entries 4,5,6,10), it was added in three portions in 10 min. Generally, dissolution of PhIO is indicative of the end of the reaction. The reaction mixture was poured onto a column of silica gel (∼20 g) and eluted with a mixture of EtOAc–petroleum ether.

4.3.2. With TEMPO/CuCl₂. (*Method A*, Table 5) *In the presence of oxygen*: To a solution of tertiary allylic alcohol (1 mmol) in CH_3CN (5 mL) were successively added TEMPO (15.6 mg, 0.1 equiv), 4 Å molecular sieves (0.15 g) and $CuCl_2\cdot 2H_2O$ (58 mg, 0.5 equiv). The brown reaction mixture was stirred at room temperature under oxygen (balloon) for a period of time indicated in Table 5. The light brown suspension was diluted with ether, washed twice with water, dried (Na_2SO_4) and evaporated under reduced pressure. The residue was purified by flash chromatography on silica gel.

(*Method B*, Table 5) *with an excess of CuCl₂*: To a solution of tertiary allylic alcohol (1 mmol) in CH_3CN (5 mL) were successively added TEMPO (15.6 mg, 0.1 equiv), 4 Å molecular sieves (0.2 g) except for **12a** (35 mg) and $CuCl_2\cdot 2H_2O$ (0.34 g, 2 equiv). The brown reaction mixture was stirred at room temperature for a period of time indicated in Table 5. The reaction mixture was worked up as indicated above.

*4.3.2.1. 3-n-Butyl-2-cyclohexen-1-one (**1b**).* EtOAc–petroleum ether (1:5), oil. ^1H NMR: 0.88 (t, 1H, J=7.1 Hz, Me), 1.2–1.53 (m, 4H, $2CH_2$), 1.95 (quintuplet, 2H, J=6.2 Hz), 2.18 (t, 2H, J=7.7 Hz, CH_2), 2.25–2.35 (m, 4H, $2CH_2$), 5.84 (s, 1H). ^{13}C NMR: 13.8, 22.3, 22.8, 29.1, 29.7, 37.4, 37.8, 125.6, 166.8, 199.9. Its spectroscopic data were in accordance with those reported in the literature.[7a]

*4.3.2.2. 3-Phenyl-2-cyclohexen-1-one (**2b**).* EtOAc–petroleum ether (1:4), solid; mp 62–63 °C (hexane) (lit.[7a] mp 64–65 °C). ^1H NMR: 2.13 (quintuplet, 2H, J=6.5 Hz, H-5), 2.27 (t, 2H, J=6.2 Hz, H-6), 2.75 (td, 2H, J=1.2, 6.2 Hz, H-4), 6.4 (t, J=1.3 Hz, H-2), 7.3–7.4 (m, 3H), 7.5–7.6 (m, 2H). ^{13}C NMR: 22.8, 28.1, 37.3, 125.4, 126.1 (2C), 128.8 (2C), 130.0, 138.8, 159.8, 199.9. Its spectroscopic data were in perfect agreement with those described in the literature.[7a]

*4.3.2.3. 3-Vinyl-2-cyclohexen-1-one (**3b**).* EtOAc–petroleum ether (1:5), yellow oil. ^1H NMR: 1.98 (quintuplet, 2H, J=6 Hz, H-5), 2.25–2.5 (m, 4H, H-4, H-6), 5.41 (d, 1H, J=10.7 Hz), 5.63 (d, 1H, J=17.5 Hz), 5.88 (s, 1H, H-2), 6.43 (dd, J=10.7, 17.4 Hz). ^{13}C NMR: 22.2, 24.3, 24.9, 37.7, 120.7, 128.2, 137.9, 156.9, 200.3. NMR data were identical with those described in the literature.[35]

*4.3.2.4. 3-Ethynyl-2-cyclohexen-1-one (**4b**).* EtOAc–petroleum ether (1:6), yellow oil. ^1H NMR: 2.20 (quintuplet, 2H, J=6 Hz, H-5), 2.25–2.42 (m, 4H, H-4, H-6), 3.54 (s, 1H), 6.24 (t, 1H, J=1.5 Hz, H-2). ^{13}C NMR: 22.5, 30.2, 37.3, 82.5, 87.2, 134.0, 142.2, 198.5. Its spectroscopic data were in accord with those described in the literature.[36]

*4.3.2.5. 3,6,6-Trimethyl-2-cyclohexen-1-one (**5b**).* EtOAc–petroleum ether (1:6), oil. ^1H NMR: 1.1 (s, 6H, 2Me), 1.8 (t, 2H, J=6.1 Hz, H-5), 1.9 (s, 3H, Me), 2.27 (t, 2H, J=6 Hz, H-4), 5.74 (sextuplet, 1H, J=1.4 Hz, H-2). ^{13}C NMR: 24.1 (Me), 24.5 (2 Me), 28.8, 36.4, 40.5, 125.4, 160.7, 204.9. NMR data were identical with those reported in the literature.[37]

*4.3.2.6. (S)-2,3-Dimethyl-5-isoprenylcyclohex-2-en-1-one (**6b**).* Ether–petroleum ether (1:7), oil, $[\alpha]_D^{20}$ +103 (c, 1.2, $CHCl_3$)lit.[38] $[\alpha]_D^{26}$ +103.5 (c, 2.1). ^1H NMR: 1.74 (s, 3H, Me), 1.76 (s, 3H, Me), 1.94 (s, 3H, Me), 2.25 (dd, 1H, J=2.7, 4.8 Hz), 2.34 (m, 2H), 2.53 (dd, 1H, J=3.8, 5.4 Hz), 2.6 (m, 1H), 4.43 (s, 1H), 4.78 (s, 1H). ^{13}C NMR: 11.1, 20.8, 21.9, 38.3, 41.6, 42.8, 110.6, 131.1, 147.2, 154.6, 199.4. Its spectroscopic data were in agreement with those described in the literature.[19a]

*4.3.2.7. 3-n-Butyl-2-cyclopenten-1-one (**7b**).* EtOAc–petroleum ether (1:5), yellow oil. ^1H NMR: 0.88 (t, 1H, J=7.1 Hz, Me), 1.2–1.41 (m, 2H), 1.45–1.6 (m, 2H), 2.32–2.40 (m, 4H), 2.51–2.55 (m, 2H), 5.88 (quintuplet, 1H, J=1.3 Hz). ^{13}C NMR: 13.8, 22.4, 29.2, 31.5, 33.2, 35.3, 129.4, 183.3, 210.1. Spectroscopic data were consistent with the literature data.[38]

*4.3.2.8. 3-Vinyl-2-cyclopenten-1-one (**8b**).* EtOAc–petroleum ether (1:4), yellow oil. ^1H NMR: 2.41 (m, 2H), 2.72 (m, 2H), 5.48 (d, 1H, J=10.5 Hz), 5.73 (d, 1H, J=17.5 Hz), 6.0 (s, H), 6.78 (dd, 1H, J=10.5, 17.5 Hz). ^{13}C NMR: 26.5, 34.7, 122.4, 131.0, 132.7, 172.1, 209.6. NMR data were consistent with those reported in the literature.[39]

*4.3.2.9. 2,3-Dimethyl-2-cyclopenten-1-one (**9b**).* EtOAc–petroleum ether (1:5), yellow oil. ^1H NMR: 1.64 (s, 3H, Me), 2.0 (s, 3H, Me), 2.31 (m, 2H), 2.44 (m, 2H). ^{13}C NMR: 8.2, 17.6, 31.9, 34.5, 136.6, 170.4, 210.3. NMR data were identical with those described in the literature.[38]

*4.3.2.10. (Z,E)-3-n-Butyl-2-cyclododecen-1-one (**10b**).* Ether–petroleum ether (5:95), oil. IR (neat): 1681, 1611 cm^{-1}. ^1H NMR (mixture of *Z,E* diastereomers): 0.92 (t, 3H, J=7.2 Hz, Me (*E*)), 0.94 (t, 3H, J=7.1 Hz, Me (*Z*)), 1.1–1.75 (m, 36H), 2.1 (t, 2H, J=7.6 Hz, CH_2 (*E*)), 2.18 (t, 2H, J=7.5 Hz, CH_2 (*Z*)), 2.39–2.48 (m, 6H, $2CH_2$ (*Z*), CH_2 (*E*)), 2.64 (t, 2H, J=6.5 Hz, CH_2 (*E*)), 6.14 (s, 1H (*E*)), 6.26 (s, 1H (*Z*)). ^{13}C NMR (mixture of *Z,E* diastereomers): 14.0, 14.1, 22.4, 22.6, 23.2, 23.4 (2C), 23.7, 24.2, 24.6, 24.7, 24.8, 25.0, 25.1, 25.3, 26.1, 26.4, 26.9, 27.1, 29.9, 31.6, 31.9, 35.8, 38.8, 41.5, 42.1, 126.1, 127.7, 156.7, 161.1, 203.1, 204.6. HRMS calcd for $C_{16}H_{28}O$ $(M)^+$ 236.2140; found: 236.2139.

*4.3.2.11. (Z,E)-2,5-Dimethyl-4-nonen-3-one (**11b**).* Ether–petroleum ether (2:98), yellow oil. IR (film): 1680, 1610 cm^{-1}. ^1H NMR (mixture of *Z,E* diastereomers): 0.91 (t, 3H, J=7 Hz, Me (*Z*)), 0.92 (t, 3H, J=7 Hz, Me (*E*)), 1.08 (d, 6H, J=7 Hz, 2Me (*Z*)), 1.09 (d, 6H, J=7 Hz, 2Me (*E*)), 1.26–1.51 (m, 8H, H-7, H-8, (*Z*, *E*)), 1.88 (d, 3H, J=1.4 Hz, Me (*Z*)), 2.13 (d, 3H, J=1.4 Hz, Me (*E*)), 2.14 (t, 2H, J=7 Hz, H-6 (*E*)), 2.14–2.68 (m, 4H, H-6 (*Z*), H-2 (*E*, *Z*)), 6.08 (br s, 1H, H-4 (*Z*)), 6.1 (q, 1H, J=1.2 Hz, H-4 (*E*)). ^{13}C NMR: 14.3, 14.5, 18.8 (4C), 19.7, 22.8, 23.3, 25.9, 30.1, 30.8, 34.0, 41.5, 41.8, 41.9, 122.3, 122.9, 159.8, 160.4, 204.8, 205.4. NMR data were in accordance with those described in the literature.[40]

*4.3.2.12. (Z,E)-3-Methyl-2-hepten-1-al (**12b**).* Ether–petroleum ether (1:5), liquid. IR (film): 1673, 1631 cm^{-1}. ^1H NMR: 0.89 (t, 1H, *J*=7.2 Hz, Me (*E*)), 0.91 (t, 1H, *J*=7.2 Hz, Me (*Z*)), 1.21–1.38 (m, 4H, H-5, H-6 (*Z*, *E*)), 1.4–1.52 (m, 4H, H-5, H-6 (*Z*, *E*)), 1.95 (s, 3H, Me (*Z*)), 2.13 (s, 3H, Me (*E*)), 2.16 (t, 2H, *J*=7.6 Hz, H-4 (*E*)), 2.55 (t, 2H, *J*=7.5 Hz, H-4 (*Z*)), 5.84 (d, 1H, *J*=8.1 Hz, H-2 (*E*)), 5.86 (d, 1H, *J*=8.1 Hz, H-2 (*Z*)), 9.93 (d, 1H, *J*=8.2 Hz, H-1 (*Z*)), 9.96 (d, 1H, *J*=8.1 Hz, H-1 (*E*)). ^{13}C NMR: 14.2 (2C), 17.8, 22.6, 22.9, 25.4, 29.6, 31.3, 32.7, 40.7, 127.6, 128.7, 164.8, 165.3, 191.1, 191.7. HRMS: calcd for $C_8H_{13}O$ $(M-H^-)^+$ 125.0966; found: 125.09645.

*4.3.2.13. Cyclohexylideneacetaldehyde (**13b**).* Ether–petroleum ether (1:6), liquid. IR (film): 1674, 1625 cm^{-1}. ^{1}H NMR: 1.64–1.76 (m, 6H), 2.3 (t, 2H, *J*=6.5 Hz), 2.71 (t, 2H, *J*=6.5 Hz), 5.82 (d, 1H, *J*=8.3 Hz), 10.02 (d, 1H, *J*=8.3 Hz). ^{13}C NMR: 26.5, 28.5, 29.0, 30.0, 38.5, 125.7, 168.6, 191.0. Its spectroscopic data were in agreement with those described in the literature.[41]

*4.3.2.14. 2-t-Butyldiphenyloxymethyl-3-methyl-2-cyclohexen-1-one (**14b**).* Ether–petroleum ether (1:6), solid: mp 61–63 °C. IR (neat): 3049, 1667, 1634 cm^{-1}. 1.04 (s, 9H, 3 Me), 1.91 (quintuplet, 2H, *J*=6.2 Hz, H-5), 1.99 (s, 3H, Me), 2.32–2.40 (m, 4H, H-6, H-4), 4.47 (s, 2H), 7.4 (m, 6H), 7.7 (m, 4H). ^{13}C NMR: 19.5, 21.5, 22.1, 27.0 (3Me), 33.1, 37.6, 56.3, 127.6 (4C), 129.6 (2C), 134.0 (2C), 134.5, 135.8 (4C), 160.5, 197.6. HRMS calcd for $C_{24}H_{31}O_2Si$ $(M+H^+)$ 379.2093; found: 379.2094.

*4.3.2.15. 3-Methyl-2-cyclohepten-2-one (**15b**).* Ether–petroleum ether (1:3), liquid. IR (film): 1652 cm^{-1}. ^{1}H NMR: 1.75–1.8 (m, 4H), 1.95 (s, 3H, Me), 2.42 (t, 2H, *J*=5.7 Hz), 2.57 (t, 2H, *J*=6.2 Hz), 5.92 (s, 1H). ^{13}C NMR: 21.8, 25.5, 28.0, 34.9, 42.9, 130.2, 159.0, 204.2. Its physical data were identical with those described in the literature.[32]

4.4. Study of the oxidative rearrangement of 1a with other reoxidants of TEMPO

4.4.1. PhI(OAc)$_2$ as a primary oxidant in the presence of Lewis acids (Table 6, entry 2). To a solution of **1a** (0.154 g, 1 mmol) in CH_2Cl_2 (3 mL) were added PhI(OAc)$_2$ (0.386 g, 1.2 equiv), TEMPO (15.6 mg, 10 mol %), Bi(OTf)$_3$ (26 mg, 4 mol %). The reaction mixture was stirred for 45 min at room temperature and poured into a column of silica gel. Elution with EtOAc–petroleum ether (5:95) gave the allylic acetate **1c** (62 mg, 32%) as an oil; IR (film):1725, 1660 cm^{-1} ^{1}H NMR: 0.88 (t, 3H, *J*=7 Hz, Me), 1.18–1.42 (m, 4H), 1.59–1.82 (m, 4H), 1.88–2 (m, 4H), 2.02 (s, 3H, Me), 5.24 (br s, 1H, CHOAc), 5.43 (br s, 1H, CH=C). ^{13}C NMR: 14.0, 19.2, 21.5, 22.4, 28.3, 28.4, 29.6, 37.3, 68.9, 119.3, 144.9, 170.9. Its NMR data were consistent with the literature data.[42] Further elution with EtOAc–petroleum ether (1:6) furnished the enone **1b** (62 mg, 41%), which NMR data were identical with those described in 4.3.1.

4.4.2. mCPBA as a primary oxidant (Table 7, entry 2). To a solution of **1a** (0.154 g, 1 mmol) in CH_2Cl_2 (3 mL) were added TEMPO (15.6 mg, 10 mol %) and *n*Bu$_4$NBr (32 mg, 10 mol %). The reaction mixture was cooled to 0 °C and Bi(OTf)$_3$ (65 mg, 10 mol %) and *m*CPBA (294 mg, 1.2 equiv) were successively added. After stirring the reaction mixture for 1 h at 0 °C, a saturated solution of $NaHCO_3$ was added. The aqueous phase was extracted once with CH_2Cl_2 and the combined organic extracts were washed once with water, dried (Na_2SO_4) and evaporated under reduced pressure. Purification of the residue on silica gel using EtOAc–petroleum ether (1:5) gave a mixture of the unsaturated ketone **1b** and of the epoxide **1d** (ratio:1/3), which structure was confirmed by NMR spectra.[38] Further elution with EtOAc–petroleum ether (1:3) afforded the rearranged epoxide **1e** (47 mg, 28%). ^{1}H NMR: 0.91 (t, 3H, *J*=7 Hz, Me), 1.15–1.9 (m, 12H), 2.26 (br s, 1H, OH), 3.14 (s, 1H, H-2), 3.99 (br s, 1H, H-1). ^{13}C NMR: 14.4, 18.7, 23.1, 27.0, 27.2, 29.5, 37.6, 61.9, 64.8, 67.4. NMR data were in good agreement with those reported in the literature.[43]

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