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ε-Caprolactone manufacture via efficient coupling Baeyer-Villiger oxidation with aerobic oxidation of alcohols

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ABSTRACT

To avoid the use of peracids oxidant or highly concentrated hydrogen peroxide which is potentially hazardous and explosive, herein, a new route to ε-caprolactone was developed in which molecule oxygen was employed as the terminal oxidant. The commercial available *N*-hydroxyphthalimide and ammonium cerium nitrate were used as the key catalysts for the increased yield of ε-caprolactone. For instance, the selectivity of ε-caprolactone was obtained 92 % with 85 % conversion of cyclohexanone which was comparable to the strategies using highly concentrated hydrogen peroxide. The sacrificed alcohols were transformed into corresponding ketones which were also valuable chemicals. Furthermore, the efficiency of the alcohols was achieved to unprecedented 52 %. The Baeyer-Villiger oxidation of various other cycloalkanones was also examined. The substituent group effect on the efficiency of sacrificed alcohols was investigated in which weak electron-donating substituent induced nearly quantitative yield of ε-caprolactone. The reaction mechanism was studied with the help of electron paramagnetic resonance which indicated the existence of a radical pathway.

Introduction

The Baeyer-Villiger (BV) oxidation is an extremely useful organic reaction in chemical industry [1–6]. For instance, ε-caprolactone produced from cyclohexanone and organic peracids is usually adopted as the monomer of polycaprolactone (PCL) which is an extensively used pharmaceutical material [7]. On the other hand, the BV oxidation also played an important role in the synthesis of various natural products [8–12]. It is always the development trend for the chemical industry that using safer, environmentally friendlier and cheaper oxidant [13]. In terms of the BV oxidation, the replacement of currently used peracids oxidant is especially urgent due to the facts that the peracids was known as hazardous (instability and shock sensitivity) and with low atomic economy. Lots of endeavors have been paid to develop the new oxidant for the replacement of the organic peracids [14–20]. Particularly speaking, hydrogen peroxide (H_2O_2) has been promoted as the potential oxidant as its only theoretical by-product is water [21,22]. In addition, H_2O_2 has given several promising reaction results in the last two decades. In 2001, BV oxidation was conducted with 35 % H_2O_2 and Sn-zeolite beta as catalyst by Corma and coworkers, in which the yield of ε-caprolactone was obtained 52 % [23,24]. Neumann et al. reported BV oxidation with 60 % H_2O_2 to give corresponding lactones with 60 ~ 88 % yield [25]. Sheldon et al. reported BV oxidation with 60 % H_2O_2 catalyzed by diphenyl diselenides, in which nearly quantitative lactones were yielded [26]. Berkessel et al. conducted BV oxidation in hexafluoroisopropanol (HFIP) and 92 % yield of ε-caprolactone was achieved [27,28]. As disclosed by the aforementioned chemists, the H_2O_2 of higher concentration generally gave an ideal oxidative performance. Unfortunately, the usage of H_2O_2 of higher concentration is not desirable for safety concerns [29]. Except for commercial available H_2O_2, the method using it generated *in situ* from aerobic oxidation of alcohols was also promoted at the mean time. Ishii et al. used *N*-hydroxyphthalimide (NHPI)/$InCl_3$ or NHPI/*p*-toluenesulfonic acid (*p*-TsOH) as catalysts and adopted cyclohexanol or benzhydrol as the sacrificed agents to conduct BV oxidation [30,31]. Our group used NHPI/ammonium cerium nitrate (CAN) to catalyzed BV oxidation with KA oil (mixture of cyclohexanol and cyclohexanone) as the substrate [32]. However, both the methods suffered a poor selectivity of lactones when the conversion of substrates increased.

In this work, we present a new method to synthesize ε-caprolactone with oxygen as the oxidant and NHPI/CAN as catalysts. The alcohols played as the sacrificed agent whose products were also valuable industrial chemicals. The new route gave a very promising result for both conversion and selectivity. The substituent group effect on the efficiency of sacrificed alcohols was investigated, as well as the corresponding radical mechanism assisted by the electron paramagnetic

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resonance (EPR) spectroscopy.

Experimental

Material

NHPI, CAN, azobisisobutyronitrile (AIBN), Galvinoxyl, TEMPO, HFIP, trifluoroethanol (TFE), biphenyl, *p*-TsOH•H_2O, DMPO, alcohols, ketones and lactones were purchased from Energy Chemical. Acetonitrile (MeCN), ethyl acetate (AcOEt), n-Butyl acetate ($AcOBu^n$), chlorobenzene (PhCl) and benzonitrile (PhCN) were purchased from Sinopharm Chemical Reagent Co., Ltd. All the reagents were used directly without further purification.

Aerobic oxidation

The aerobic oxidation proceeded in a 50 mL round bottom with a magnetic stirring bar in it. In the 1st step, certain amount of NHPI and AIBN were mixed with certain amount of cyclohexanone and benzhydrol (6 mmol, 1.1 g) in AcOEt (3 mL), the flask was purged with pure oxygen for three times by a membrane pump, after which it was heated to 75 °C by oil bath for 22 h. In the 2nd step, the temperature of reaction solution was lowered to 45 °C and certain amount of CAN and HFIP (20 g, 12.5 mL) were added and stirred under oxygen for 10 h. The reaction was analyzed by a Shimadzu gas chromatography instrument (GC-2010) which was equipped with a capillary column (HP-1, 30 m length, 0.25 mm diameter, 0.25 μm film) and a FID detector. Biphenyl was used as the internal standard compound. GC-MS tests were conducted with a Shimadzu GCMS-QP2010 instrument.

Rearrangement of peroxide intermediate

The 1, 1′-peroxybis (cyclohexan-1-ol) was synthesized according to previous paper [59]. The rearrangement of 1, 1′-peroxybis (cyclohexan-1-ol) proceeded in a 25 mL single-necked flask with round bottom. The 0.05 g peroxide and 0.0017 g (4 mol%) *p*-TsOH•H_2O were added into 5 mL degassed HFIP, and the reaction mixture was stirred intensively with a magnetic stir bar under 25 °C. A Shimadzu high performance liquid chromatography (HPLC) equipped with shim-pack VP-ODS C18 column (4.6 mm × 250 L, 5 μm) was used to quantify the amount of unreacted substrate.

Characterization of intermediate

The H_2O_2 measurement was performed according to previous paper [60]. The EPR spectrum was recorded by a Bruker cw-EPR spectrometer (A300) at X band. The modulation frequency was 100 KHz and power of microwave was 2 mw. 20 μL reaction solutions was adopted at certain time and mixed with DMPO solution (0.1 M in phosphate buffer saline) of equivalent volume. After shaking for 5 min, the mixture was injected into a capillary and tested at room temperature. Elemental analysis result was obtained by Elementar Vario MICRO cube. The nuclear magnetic resonance (NMR) tests were conducted on Bruker AVANCE III 500 instrument, ^1H NMR at 500 MHz and ^{13}C NMR at 125 MHz.

Results and discussion

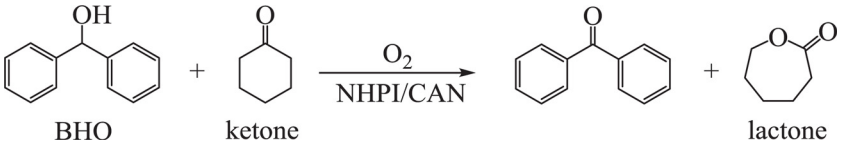
BV oxidation with benzhydrol (BHO) using NHPI-mediate CAN as catalyst

For the important application in producing ε-caprolactone, we chose cyclohexanone as the model substrate. Table 1 presents the results of BV oxidation of cyclohexanone with BHO as the sacrificed alcohol (Scheme 1). Under the most optimized conditions (Entry 2), the selectivity of ε-caprolactone maintained 92 % with 85 % conversion of cyclohexanone. The efficiency of alcohol was 52 % (based on the definition of ε-caprolactone production amount / BHO consumption amount × 100 %) which was superior to former strategy (37 % efficiency of alcohol with 55 % yield of ε-caprolactone) [30,31]. When the amount of catalyst decreased to 5 mol% (Entry 1), the efficiency of alcohol dramatically lowered to 42 % which was attributed to the low conversion of substrate. On the other hand, the efficiency of alcohol was not significantly improved with the increase of catalyst addition (Entry 3), also, the selectivity showed obviously decrease. Based on previous work [27,28], this result could be due to the side reaction induced by the excessive catalyst. Next, we had examined the effect of the ratio of alcohol and substrate on the BV oxidation (Entries 4–7). As expected, the higher efficiency of alcohol was achieved when the addition amount of cyclohexanone increased (Entries 4–6) which leaded to the increasing accessibility of cyclohexanone for H_2O_2 *in situ* produced from the aerobic oxidation of BHO. Unfortunately, an unwanted reaction of cyclohexanone happened which limited the further addition of cyclohexanone (Entry 4) [32]. When the initial concentration of cyclohexanone was low, the efficiency of alcohol and selectivity of ε-caprolactone were both unsatisfactory (Entry 7). This result could be explained as the higher amount of water which was harmful to the reaction was produced from the self-decomposition of H_2O_2 which could not be timely used by the insufficient cyclohexanone. The HFIP was chosen as the, solvent for BV oxidation. As reported by former literatures [27,28,30–32], the HFIP was proved to be irreplaceable (Entry 13). Furthermore, the ratio of the two solvents obviously affected the result of the BV oxidation (Entries 8, 9). In terms of the catalysts (Entries 10, 11), we had attempted the *p*-TsOH to catalyze the second step which was apparently inferior compared with CAN (Entry 12). Surprisingly, as effective as BHO, benzyl alcohol showed promising result which 86 % selectivity of ε-caprolactone was obtained with 72 %

Table 1
BV oxidation of cyclohexanone to ε-caprolactone under various conditions with BHO[a].

Entry	Catal.mol/%[b]	BHO/ ketone initial ratio	Conv. Ketone/ %	Sel. Lactone/ %[c]	Conv. BHO/ %	Alcohol efficiency/ %[d]
1	5	1.5	66	96	99	42
2	7.5	1.5	85	92	99	52
3	10	1.5	96	73	99	47
4	7.5	0.6	45	79	99	59
5	7.5	1	72	75	99	54
6	7.5	2	95	74	99	35
7	7.5	3	96	69	99	22
8[e]	7.5	1.5	81	85	99	46
9[f]	7.5	1.5	84	92	99	51
10[g]	0	1.5	61	36	99	15
11[h]	0	1.5	Trace	0	0	–
12[i]	7.5	1.5	84	41	99	23
13[j]	7.5	1.5	78	26	99	14
14[k]	7.5	1.5	72	86	81[l]	51

[a] General conditions, 1st step, NHPI/AIBN, BHO 6 mmol, certain amount of cyclohexanone in AcOEt 3 mL, O_2 1 atm, 75 °C, 600 rpm, 22 h; 2nd step, add CAN and 20 g HFIP, 45 °C, continue reaction for 10 h. Reaction was monitored by GC, biphenyl was used as internal standard compound.
[b] Based on BHO amount.
[c] Sel. Lactone% = ε-caprolactone production amount / cyclohexanone consumption amount × 100 %.
[d] Alcohol efficiency/% = ε-caprolactone production amount / BHO consumption amount × 100 %.
[e] HFIP 15 g.
[f] HFIP 30 g.
[g] 10 mol% NHPI, 0 mol% CAN.
[h] 0 mol% NHPI, 10 mol% CAN.
[i] 10 mol% *p*-TsOH•H_2O was used instead of CAN.
[j] HFIP 0 g, TFE 20 g.
[k] Benzyl alcohol was used instead of BHO.
[l] Conversion of benzyl alcohol.



Scheme 1. BV oxidation of cyclohexanone to ε-caprolactone with BHO.

Table 2
Solvent effect on the BV oxidation of cyclohexanone with BHO[a].

Entry	Solvent	Conv. Ketone/%	Sel. Lactone/%[b]
1	AcOEt	85	92
2	AcOBu^n	79	91
3	MeCN	82	78
4	PhCN	94	74
5	PhCl	87	89

[a] General conditions, BHO 6 mmol, cyclohexanone 4 mmol, Catal. mol % = 7.5 mol% (based on BHO), O_2 1 atm, 600 rpm, solvent 3 mL, 75 °C 22 h, then add HFIP 20 g, 45 °C 10 h.
[b] Sel. Lactone/% = ε-caprolactone production amount / cyclohexanone consumption amount × 100 %.

transformation of the substrate (Entry 14). One other thing to note was that none H_2O_2 was detected when the aerobic oxidation of BHO was conducted with the fluorinated alcohol in presence. Thus, the strategy was separated into two steps that fluorinated alcohol was added after the aerobic oxidation of alcohols was completed. As for the products achievement, the significant boiling points difference of different components should facilitate the distillation separation.

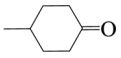
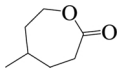
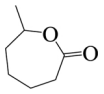
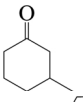
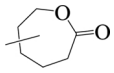
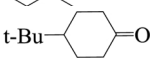
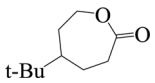
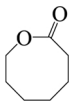
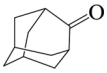
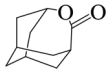
The choice of solvent for the aerobic oxidation of alcohol is also crucial not only for the aerobic oxidation of alcohols but also for the subsequent BV oxidation. We conducted the strategy in several different solvents (Table 2). Compared with AcOEt (Entry 1), the conversion of substrate was slightly lower, along with a similar selectivity of ε-caprolactone in AcOBu^n (Entry 2). Although the MeCN was reported as a favorable solvent for H_2O_2 production [33], its selectivity of BV product was significantly poor in our strategy (Entry 3). Similarly, PhCN gave an unsatisfactory result with 74 % selectivity, although the transformation of cyclohexanone was enhanced (Entry 4). The PhCl gave an unexpected result which 89 % selectivity of ε-caprolactone was obtained while 87 % of cyclohexanone was converted (Entry 5). Former researchers examined the PhCl as an inferior solvent because the aerobic oxidation of alcohol (production of H_2O_2) proceeded slowly in it [33]. We speculated PhCl somewhat favored the BV oxidation with low concentration of H_2O_2.

Based on above results, various cycloalkanones were reacted under similar conditions (Table 3). The cyclopentanone was the most frequently used model substrate for BV reaction as the strained ring greatly facilitated the key rearrangement process [34–36]. As can be seen, the cyclopentanone gave 93 % selectivity of δ-valerolactone with 99 % conversion (Entry 1). We had investigated the effect of substituent group on the substrates. The weak electron-donating methyl group slightly improved the selectivity to 85–86 % (Entries 3–5), while the substrate was almost quantitatively transformed into lactone under the tertiary butyl group circumstances (Entry 6). The cycloheptanone was also examined, which gave 69 % selectivity of oxocan-2-one while 75 % of substrate was converted (Entry 7). Other cycloalkanones like 2-norbornanone and adamantanone were oxidized then, which both led to satisfactory yields (Entries 8, 9).

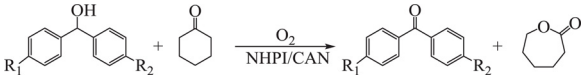
Substituent group effect on the efficiency of BV oxidation

As the source of *in situ* H_2O_2, the aerobic oxidation of alcohols was assumed to seriously affect the efficiency of the BV reaction (Scheme 2). Table 4 showed the reaction results with different alcohols under same conditions. When the alcohol was decorated with weak electron-donating group like methyl group, the superior selectivity of ε-caprolactone was obtained along with a high conversion of substrate (Entry 2). We speculated the weak electron-donating group facilitated the breakage of the C—H bond of alcohol which was supposed to be the rate determining step of the oxidation reaction [37,38]. On the contrary, the BV oxidation dramatically deteriorated when alcohol with electron-withdraw groups was used (Entries 3–7). These results could be attributed to the reluctance of the aerobic oxidation of the alcohols, which clearly lesser substrates were oxidized under the same conditions. We also conducted the alcohol effect experiment with a benzyl alcohol series (see supplementary material, Table S1). To our surprise, the electron-donating group did not increase the efficiency of BV oxidation but induced the side reaction between H_2O_2 and aldehydes

Table 3
BV oxidation of cycloalkanones to lactones with BHO using NHPI/CAN as catalyst[a].

Entry	Cycloalkanones	Lactones	Conv. Cycloalkanones/ %	Sel. Lactones/ %[b]
1			99	93
2			85	92
3			85	97
4			85	97
5			86	96
6			93	95
7			75	69
8			98	95
9			99	99

[a] General conditions, BHO 6 mmol, cycloalkanone 4 mmol, Catal.mol % = 7.5 mol% (based on BHO), O_2 1 atm, 600 rpm, AcOEt 3 mL, 75 °C 22 h, then add HFIP 20 g, 45 °C 10 h.
[b] Sel. Lactones/% = Lactones production amount / cycloalkanones consumption amount × 100 %.



Scheme 2. Substituent group effect on the efficiency of BV oxidation.

Table 4
Substituent group effect on the BV oxidation of cyclohexanone to ε-caprolactone with BHO[a].

Entry	Alcohols	Conv. Ketone/%	Sel. Lactone/%[b]	Conv. Alcohols/%	Alcohol efficiency/%[c]
1	R_1 = H; R_2 = H	85	92	99	52
2	R_1 = CH_3; R_2 = CH_3	93	98	99	61
3	R_1 = Cl; R_2 = H	69	81	85	44
4	R_1 = Cl; R_2 = Cl	68	73	83	40
5	R_1 = F; R_2 = F	70	66	81	38
6	R_1 = CF_3; R_2 = H	71	75	88	40
7	R_1 = CN; R_2 = CN	69	72	85	40

[a] General conditions, alcohol 6 mmol, cyclohexanone 4 mmol, Catal.mol% = 7.5 mol% (based on alcohol), O_2 1 atm, 600 rpm, AcOEt 3 mL, 75 °C, 22 h, HFIP 20 g, 45 °C, 10 h. Reaction was monitored by GC, biphenyl was used as internal standard compound.
[b] Sel. Lactone/% = ε-caprolactone production amount / cyclohexanone consumption amount × 100 %.
[c] Alcohol efficiency/% = ε-caprolactone production amount / alcohol consumption amount × 100 %.

obtained from oxidation of alcohols [39,40]. The existence of the phenols as the by-products of the side reactions was proved by GC-MS spectroscopy (see supplementary material, Fig. S17). However, these side reactions would not happen when electron-withdrawing groups were in presence.

EPR evidences for the radical mechanism of BV oxidation

Considering the unique properties of HFIP including strong hydrogen bond donation ability, non-nucleophilicity, and high ionizing power [41–43], former researchers usually proposed ion involved mechanism for the rearrangement process of the BV oxidation [31]. To obtain insight into the reaction mechanism, we had conducted 2, 2, 6, 6-tetramethylpiperidine-*N*-oxyl (TEMPO) addition experiment (Fig. 1), in which the reaction was totally inhibited and none ε-caprolactone was observed [44,45]. This result inferred that radical intermediates maybe involved in the pathway. Moreover, we have conducted the inhibition experiment with another well-known radical scavenger, Galvinoxyl [46–48], which gave similar inhibition results and confirmed the radical nature of the mechanism.

The direct evidences of the presence of radical intermediates were provided by the EPR tests with the help of spin trap technique using 5, 5-dimethyl-1-pyrroline N-oxide (DMPO) as the spin trap agent [49]. As shown in Fig. 2, a clear signal of nitroxide of hydroperoxyl (OOH) radical-DMPO adduct was observed (g = 2.006, a_N = 14.0 G, $a_{H\beta}$ = 11.4 G, $a_{H\gamma}$ = 1.5 G) when the spin trap agent (DMPO) was

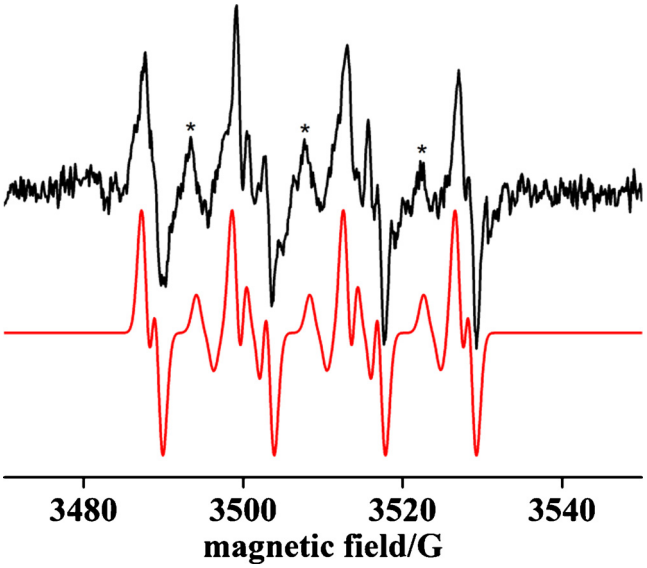


Fig. 2. EPR spectrum of the DMPO-OOH adduct. Black line was experimental spectrum, and red line was simulation spectrum, peaks with asterisk were assigned to DMPO-double adduct produced simultaneously.

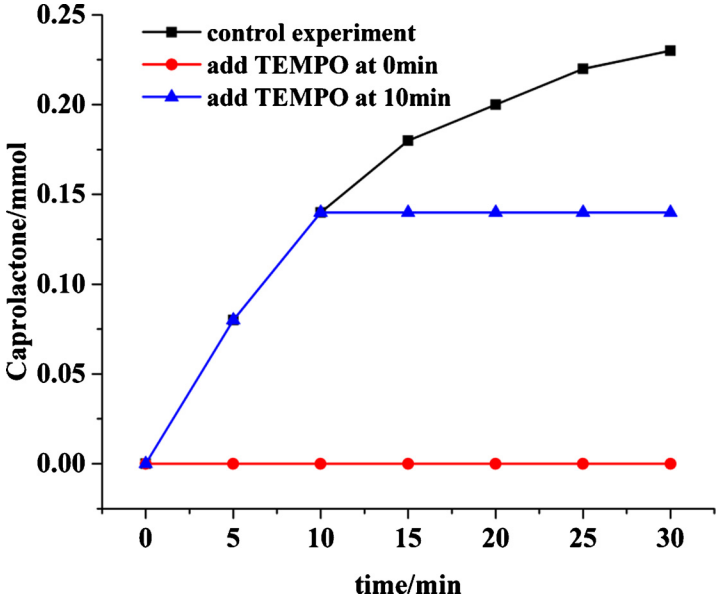


Fig. 1. TEMPO inhibition effect during the rearrangement of 1, 1′-dihydroxydicycloalkyl peroxide intermediate in HFIP.

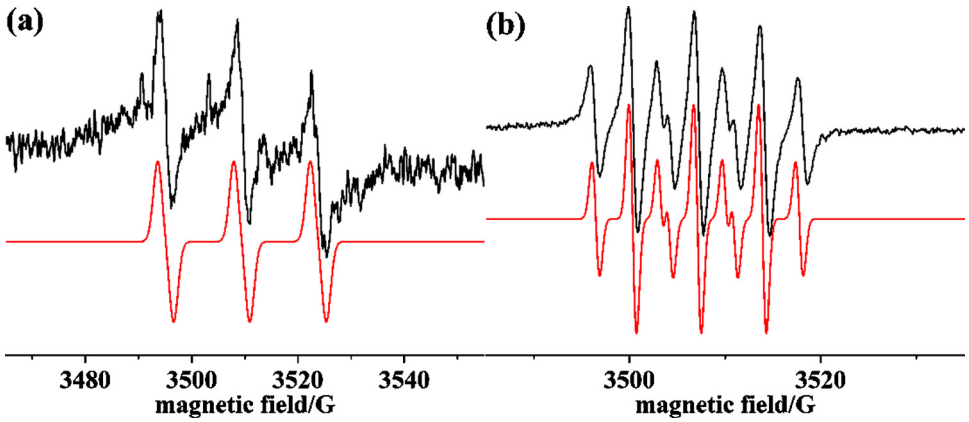
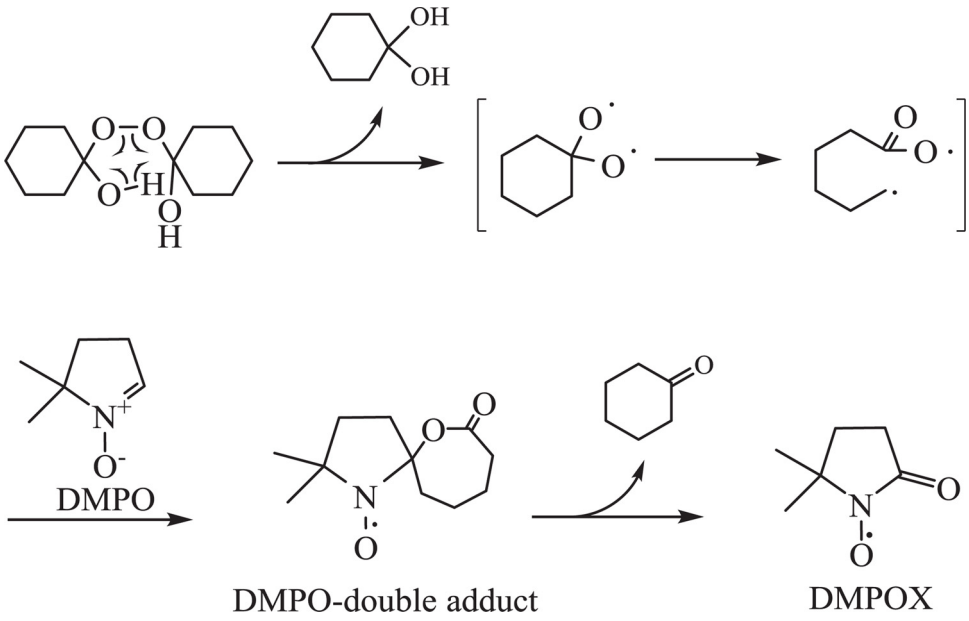


Fig. 3. EPR spectrum of (a) the DMPO-double adduct, (b) the DMPOX species derived from DMPO-double adduct. Black line was experimental spectrum, and red line was simulation spectrum.



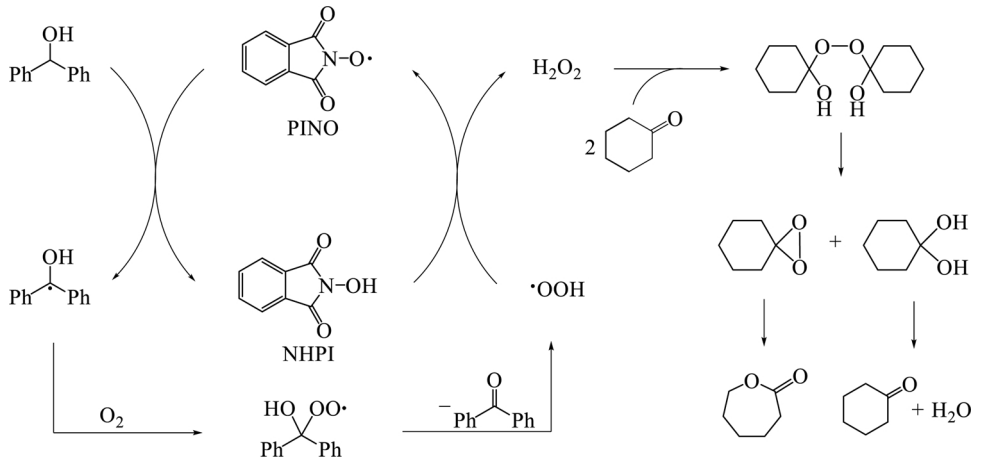
Scheme 3. Proposed spin trap adducts for BV oxidation by DMPO.

added during the first step of the reaction [50]. Based on previous literatures [51–53], the OOH was most likely released from the aerobic oxidation of the alcohol, which further abstracted a hydrogen atom and turned into H_2O_2. Meanwhile, a weak triplet signal (Fig. 2, peaks with asterisk) was also mixed within the OOH signal (g = 2.005, a_N = 14.4 G, $a_{H\gamma}$ = 1.5 G) which was existed as the only signal when the addition of DMPO was carried out at the second step of the reaction (Fig. 3 (a)). We speculated this radical species maybe the key intermediate during the rearrangement of 1, 1′-peroxybis (cyclohexan-1-ol) to ε-caprolactone. Referring to the tabulated spin trap results [50], the triplet peaks were carefully assigned to a double adduct of DMPO (Scheme 3). The further support for this assignment was its variation which transferred into the DMPOX with the prolongation of the spin trap time as shown in Fig. 3 (b) (g = 2.007, a_N = 6.8 G, a_H = 3.9 G (2 H)), which was a typical derivation signal from double adduct of DMPO as reported by former literatures (Scheme 3) [54]. Finally, we had synthesized the possible intermediate, 1, 1′-peroxybis (cyclohexan-1-ol), and conducted the EPR experiment in HFIP which gave similar spin trap results as above mentioned in the second step. It was noted that the spin traps did not show significant effect on the catalysis system including NHPI and CAN.

To summarize, the mechanism was proposed as follows (Scheme 4). In the first place, the phthalimide-*N*-oxyl radical (PINO) abstracted a hydrogen atom from the allylic position of the BHO which gave the 1-hydroxy-1, 1-diphenylmethyl radical and NHPI. The new generated radical was facile to react with molecular oxygen to form the peroxide radical which tended to liberate an OOH radical and a benzophenone. After a hydrogen atom transfer from NHPI to the OOH radical, the H_2O_2 for following BV oxidation was produced. As proposed by Ishii et al., we assumed the generation of ε-caprolactone was *via* the 1, 1′-peroxybis (cyclohexan-1-ol) intermediate [31]. However, as suggested by EPR detection, the rearrangement of this intermediate also happened in a radical mechanism. For its known high activity, the dioxirane produced from the 1, 1′-peroxybis (cyclohexan-1-ol) instantly rearranged to ε-caprolactone [55–58], while at the mean time a cyclohexanone was regenerated from the cyclohexanone hydrate.

Conclusions

In conclusion, we have developed an alternative route to ε-caprolactone using molecular oxygen as the terminal oxidant, with commercial available NHPI-mediated CAN as catalyst. The produced by-product ketones were also valuable industrial chemicals, and if necessary, could be reduced back to the original alcohols through the sophisticated hydrogenation reaction [61–65]. A satisfactory reaction result (92 % selectivity of ε-caprolactone with 85 % conversion of



Scheme 4. Proposed mechanism for BV oxidation of cyclohexanone with the aerobic oxidation of BHO.

cyclohexanone) was achieved. From the efficiency point of view, this strategy has greatly facilitated the usage of molecular oxygen in the BV oxidation. The investigation of substituent group effect and mechanism helped us to gain deeper insight into the reaction. Unfortunately, the usage of the expensive solvent (HFIP) is still the main drawback of the *in situ* H_2O_2 strategies whose replacement with cheap solvent is underway in our lab.

Declarations of interest

The authors declare no competing financial interest.

CRediT authorship contribution statement

Renfeng Du: Investigation, Writing - original draft. **Haoran Yuan:** Investigation. **Chenxuan Zhao:** Formal analysis. **Yongtao Wang:** Formal analysis. **Jia Yao:** Conceptualization, Writing - review & editing. **Haoran Li:** Supervision, Writing - review & editing.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.mcat.2020.110947.

References

[1] W.B. Fisher, J.F. Van Peppen, J.L. Kroshwite, M. Home-Grant (Eds.), Kirk-Othmer Encyclopedia of Chemical Technology, fourth ed., John Wiley and Sons, New York, 1995, pp. 851–859.
[2] A. Baeyer, V. Villiger, Einwirkung des caro'schen reagens auf ketone, Ber. Dtsch. Chem. Ges. 32 (1899) 3625–3633, https://doi.org/10.1002/cber.189903203151.
[3] A. Baeyer, V. Villiger, Ueber die einwirkung des caro'schen reagens auf ketone, Ber. Dtsch. Chem. Ges. 33 (1900) 858–864, https://doi.org/10.1002/cber.190003301153.
[4] M. Renz, B. Meunier, 100 years of Baeyer-Villiger oxidations, Eur. J. Org. Chem. 4 (1999) 737–750, https://doi.org/10.1002/(SICI)1099-0690(199904)1999:4<737::AID-EJOC737>3.0.CO;2-B.
[5] J.H. Teles, I. Hermans, G. Franz, R.A. Sheldon, Oxidation, Ullman's Encyclopedia of Industrial Chemistry, Wiley-VCH, Weinheim, 2015, p. 5 18.
[6] G.R. Krow, B.M. Trost (Ed.), Comprehensive Organic Synthesis, Pergamon Press, New York, 1991, pp. 671–688.
[7] T. Michael, E.I. Musser, Ullman's Encyclopedia Industrial Organic Chemicals, Wiley-VCH, Weinheim, 1999, pp. 1807–1823.
[8] M.E. Jung, L. Zeng, T. Peng, H. Zeng, Y. Le, J. Su, Total synthesis of Bao Gong Teng A, a natural antiglaucoma compound, J. Org. Chem. 57 (1992) 3528–3530, https://doi.org/10.1021/jo00039a005.
[9] G.R. Pettit, T.R. Kasturi, Steroids and related natural products. VIII. Synthesis of oxasteroids, J. Org. Chem. 26 (1961) 4557–4563, https://doi.org/10.1021/jo01069a087.
[10] E.J. Tisdale, C. Chowdhury, B.G. Vong, H. Li, E.A. Theodorakis, Regioselective synthesis of the bridged tricyclic core of garcinia natural products via intramolecular aryl acrylate cycloadditions, Org. Lett. 4 (2002) 909–912, https://doi.org/10.1021/ol017278w.
[11] N. Tibrewal, P. Pahari, G. Wang, M.K. Kharel, C. Morris, T. Downey, Y. Hou, T.S. Bugni, J. Rohr, Baeyer-Villiger C-C bond cleavage reaction in gilvocarcin and jadomycin biosynthesis, J. Am. Chem. Soc. 134 (2012) 18181–18184, https://doi.org/10.1021/ja3081154.
[12] F.W.J. Demnitz, C. Philippini, R.A. Raphael, Unexpected rearrangement in the peroxytrifluoroacetic acid-mediated Baeyer-Villiger oxidation of trans-3-hydroxy-4,4,10-trimethyl-9-decalone forming a 7-oxabicyclo[2.2.1]heptane. Structure proof and total synthesis of (+-)-farnesiferol-c, J. Org. Chem. 60 (1995) 5114–5120, https://doi.org/10.1021/jo00121a032.
[13] P.T. Anastas, J.C. Warner, Green Chemistry: Theory and Practice, Oxford University Press, Oxford, 1998.
[14] C. Bolm, G. Schlingloff, K. Weickhardt, Use of molecular oxygen in the Baeyer-Villiger oxidation the influence of metal catalysts, Tetrahedron Lett. 34 (1993) 3405–3408, https://doi.org/10.1016/S0040-4039(00)79167-2.
[15] M. Hamamoto, K. Nakayama, Y. Nishiyama, Y. Ishii, Oxidation of organic substrates by a molecular oxygen/aldehyde/heteropolyoxometalate system, J. Org. Chem. 58 (1993) 6421–6425, https://doi.org/10.1021/jo00075a043.
[16] T. Yamada, K. Takahashi, K. Kato, T. Takai, S. Inoki, T. Mukaiyama, The Baeyer-Villiger oxidation of ketones catalyzed by nickel (II) complexes with combined use of molecular oxygen and an aldehyde, Chem. Lett. 20 (1991) 641–644, https://doi.org/10.1246/cl.1991.641.
[17] S.I. Murahashi, Y. Oda, T. Naota, Fe2O3-catalyzed Baeyer-Villiger oxidation of ketones with molecular oxygen in the presence of aldehydes, Tetrahedron Lett. 33 (1992) 7557–7560, https://doi.org/10.1016/S0040-4039(00)60823-7.
[18] K. Kaneda, S. Ueno, T. Imanaka, Catalysis of transition metal-functionalized hydrotalcites for the Baeyer-Villiger oxidation of ketones in the presence of molecular oxygen and benzaldehyde, J. Mol. Cata. A: Chem. 102 (1995) 135–138, https://doi.org/10.1016/1381-1169(95)00055-0.
[19] E.-Y. Jeong, M.B. Ansari, S.-E. Park, Aerobic Baeyer-Villiger oxidation of cyclic ketones over metalloporphyrins bridged periodic mesoporous organosilica, ACS Catal. 1 (2011) 855–863, https://doi.org/10.1021/cs200163r.
[20] L. Wang, Y. Wang, R. Du, R. Dao, H. Yuan, C. Liang, J. Yao, H. Li, N-Hydroxyphthalimide (NHPI) promoted aerobic Baeyer-Villiger oxidation in the presence of aldehydes, ChemCatChem 10 (2018) 4947–4952, https://doi.org/10.1002/cctc.201801165.
[21] R. Noyori, M. Aoki, Green oxidation with aqueous hydrogen peroxide, Chem. Comm. 16 (2003) 1977–1986, https://doi.org/10.1039/B303160H.
[22] J. Piera, J.-E. Bäckvall, Catalytic oxidation of organic substrates by molecular oxygen and hydrogen peroxide by multistep electron transfer-a biomimetic approach, Angew. Chem. Int. Ed. 47 (2008) 3506–3523, https://doi.org/10.1002/anie.200700604.
[23] A. Corma, L.T. Nemeth, M. Renz, S. Valencia, Sn-zeolite beta as a heterogeneous chemoselective catalyst for Baeyer-Villiger oxidations, Nature 412 (2001) 423–425, https://doi.org/10.1038/35086546.
[24] A. Corma, M.T. Navarro, L. Nemeth, M. Renz, Sn-MCM-41-a heterogeneous selective catalyst for the Baeyer-Villiger oxidation with hydrogen peroxide, Chem. Comm. 21 (2001) 2190–2191, https://doi.org/10.1039/b105927k.
[25] K. Neimann, R. Neumann, Activation of hydrogen peroxide: selective oxidation reactions in perfluorinated alcohol solvents, Org. Lett. 2 (2000) 2861–2863, https://doi.org/10.1021/ol006287m.

[26] G.J. ten Brink, J.-M. Vis, I.W.C.E. Arends, R.A. Sheldon, Selenium-catalyzed oxidations with aqueous hydrogen peroxide. 2. Baeyer-Villiger reactions in homogeneous solution, J. Org. Chem. 66 (2001) 2429–2433, https://doi.org/10.1021/jo0057710.
[27] A. Berkessel, M.R.M. Andreae, Efficient catalytic methods for the Baeyer-Villiger oxidation and epoxidation with hydrogen peroxide, Tetrahedron Lett. 42 (2001) 2293–2295, https://doi.org/10.1016/S0040-4039(01)00141-1.
[28] A. Berkessel, M.R.M. Andreae, H. Schmickler, J. Lex, Baeyer-Villiger oxidations with hydrogen peroxide in fluorinated alcohols: lactone formation by a nonclassical mechanism, Angew. Chem. Int. Ed. 41 (2002) 4481–4484, https://doi.org/10.1002/1521-3773(20021202)41:23<4481::AID-ANIE4481>3.0.CO;2-7.
[29] For international regulations, see Regulations Concerning the International Carriage of Dangerous Goods by Rail (RID), European Agreement Concerning the International Carriage of Dangerous Goods by Road (ADR), and International Civil Aviation Organization Technical Instructions for the Safe Transport of Dangerous Goods by Air (ICAO TI).
[30] O. Fukuda, S. Sakaguchi, Y. Ishii, A new strategy for catalytic Baeyer-Villiger oxidation of KA-oil with molecular oxygen using N-hydroxyphthalimide, Tetrahedron Lett. 42 (2002) 3479–3481, https://doi.org/10.1016/S0040-4039(01)00469-5.
[31] K. Kamae, Y. Obora, Y. Ishii, Baeyer-Villiger oxidation of cycloalkanones with in situ generated hydrogen peroxide from alcohols and molecular oxygen using NHPI as a key catalyst, Bull. Chem. Soc. Jpn. 82 (2009) 891–895, https://doi.org/10.1246/bcsj.82.891.
[32] R. Du, H. Yuan, J. Yao, H. Li, Oxidation of KA oil to caprolactone with molecular oxygen using N-hydroxyphthalimide-mediated Ce(NH4)2(NO3)6 catalyst, Mol. Catal. 467 (2019) 24–29, https://doi.org/10.1016/j.mcat.2019.01.013.
[33] T. Iwahama, S. Sakaguchi, Y. Ishii, Production of hydrogen peroxide via aerobic oxidation of alcohols catalyzed by N-hydroxyphthalimide, Org. Process Res. Dev. 4 (2000) 94–97, https://doi.org/10.1021/op990082f.
[34] J. Fischer, W.F. Hölderich, Baeyer-Villiger-oxidation of cyclopentanone with aqueous hydrogen peroxide by acid heterogeneous catalysis, Appl. Catal. A Gen. 180 (1999) 435–443, https://doi.org/10.1016/S0926-860X(98)00378-0.
[35] M.Y. Rios, E. Salazar, H.F. Olivo, Chemo-enzymatic Baeyer-Villiger oxidation of cyclopentanone and substituted cyclopentanones, J. Mol. Cata. B: Enzy. 54 (2008) 61–66, https://doi.org/10.1016/j.molcatb.2007.12.012.
[36] S. Ueno, K. Ebitani, A. Ookubo, K. Kaneda, The active sites in the heterogeneous Baeyer-Villiger oxidation of cyclopentanone by hydrotalcite catalysts, Appl. Surf. Sci. 121 (1997) 366–371, https://doi.org/10.1016/S0169-4332(97)00334-6.
[37] T. Iwahama, S. Sakaguchi, Y. Nishiyama, Y. Ishii, Aerobic oxidation of alcohols to carbonyl compounds catalyzed by N-hydroxyphthalimide (NHPI) combined with Co(acac)3, Tetrahedron Lett. 36 (1995) 6923–6926, https://doi.org/10.1016/0040-4039(95)01431-G.
[38] R. Liu, X. Liang, C. Dong, X. Hu, Transition-metal-free: A highly efficient catalytic aerobic alcohol oxidation process, J. Am. Chem. Soc. 126 (2004) 4112–4113, https://doi.org/10.1021/ja031765k.
[39] M. Matsumoto, H. Kobayashi, Y. Hotta, Intramolecular [4+2] cycloadditions of nitrosoalkenes with olefins, J. Org. Chem. 49 (1984) 4741–4743, https://doi.org/10.1021/jo00198a038.
[40] K. Sato, M. Hyodo, J. Takagi, M. Aoki, R. Noyori, Hydrogen peroxide oxidation of aldehydes to carboxylic acids: An organic solvent-, halide- and metal-free procedure, Tetrahedron Lett. 41 (2000) 1439–1442, https://doi.org/10.1016/S0040-4039(99)02310-2.
[41] L. Eberson, O. Persson, M.P. Hartshorn, Detection and reactions of radical cations generated by photolysis of aromatic compounds with tetranitromethane in 1, 1, 1, 3, 3, 3-hexafluoro-2-propanol at room temperature, Angew. Chem. Int. Ed. Engl. 34 (1995) 2268–2269, https://doi.org/10.1002/anie.199522681.
[42] L. Eberson, M.P. Hartshorn, O. Persson, F. Radner, Making radical cations live longer, Chem. Comm. 18 (1996) 2105–2112, https://doi.org/10.1039/P29950001735.
[43] B. Elsler, A. Wiebe, D. Schollmeyer, K.M. Dyballa, R. Franke, S.R. Waldvogel, Source of selectivity in oxidative cross-coupling of aryls by solvent effect of 1, 1, 1, 3, 3, 3-hexafluoropropan-2-ol, Chem. Eur. J. 21 (2015) 12321–12325, https://doi.org/10.1002/chem.201501604.
[44] W.B. Liu, D.P. Schuman, Y.F. Yang, A.A. Toutov, Y. Liang, H.F.T. Klare, N. Nesnas, M. Oestreich, D.G. Blackmond, S.C. Virgil, S. Banerjee, R.N. Zare, R.H. Grubbs, K.N. Houk, B.M. Stoltz, Potassium tert-butoxide-catalyzed dehydrogenative C–H silylation of heteroaromatics: a combined experimental and computational mechanistic study, J. Am. Chem. Soc. 139 (2017) 6867–6879, https://doi.org/10.1021/jacs.6b13031.
[45] N.D. Schley, G.C. Fu, Nickel-catalyzed Negishi arylations of propargylic bromides: a mechanistic investigation, J. Am. Chem. Soc. 136 (2014) 16588–16593, https://doi.org/10.1021/ja508718m.
[46] G.W. Kabalka, H.C. Brown, A. Suzuki, S. Honma, A. Arase, M. Itoh, Inhibition of the reaction of organoboranes with. α, β-unsaturated carbonyl derivatives by Galvinoxyl. Evidence for a free-radical chain mechanism, J. Am. Chem. Soc. 92 (1970) 710–712, https://doi.org/10.1021/ja00706a054.
[47] P.D. Bartlett, T. Funahashi, Galvinoxyl (2, 6-di-tert-butyl-α-(3, 5-di-tert-butyl-4-oxo-2, 5-cyclohexadiene-1-ylidene)-p-tolyloxy) as a scavenger of shorter-lived free radicals, J. Am. Chem. Soc. 84 (1962) 2596–2601, https://doi.org/10.1021/ja00706a054.
[48] E.G. Janzan, C.A. Evans, Y. Nishi, Kinetic study of radical production in the thermal decomposition of benzoyl peroxide by electron spin resonance spin trapping (spin counting). Rate (and substituent effect on the rate) of spin trapping by competitive scavenging of benzoyloxy radicals with Galvinoxyl, J. Am. Chem. Soc. 94 (1972) 8236–8238, https://doi.org/10.1021/ja00778a053.
[49] J.E. Wertz, J.R. Bolton, Electron Spin Resonance: Elementary Theory and Practical Applications, McGraw-Hill, New York, 1972.
[50] G.R. Buettner, Spin trapping: ESR parameters of spin adducts 1474 1528V, Free Radic. Biol. Med. 3 (1987) 259–303, https://doi.org/10.1016/S0891-5849(87)80033-3.
[51] E.G. Moskvitina, S.V. Puchkov, I.M. Borisov, A.L. Perkel, Equilibrium between the hydroperoxyl and 1-hydroxycyclohexylperoxyl radicals-chain carriers in cyclohexanol oxidation with molecular oxygen, React. Kinet. Catal. Lett. 54 (2013) 538–544, https://doi.org/10.1134/S0023158413050121.
[52] C. Chang, X. Yang, B. Long, J. Li, A water-promoted mechanism of alcohol oxidation on a Au (111) surface: understanding the catalytic behavior of bulk gold, ACS Catal. 3 (2013) 1693–1699, https://doi.org/10.1021/cs400344r.
[53] E.G. Janzen, D.E. Nutter Jr., E.R. Davis, B.J. Blackburn, On spin trapping hydroxyl and hydroperoxyl radicals, Can. J. Chem. 56 (1978) 2237–3342, https://doi.org/10.1139/v78-368.
[54] K. Makino, A. Hagi, H. Ide, A. Murakami, M. Nishi, Mechanistic studies on the formation of aminoxyl radicals from 5, 5-dimethyl-1-pyrroline-N-oxide in fenton systems. Characterization of key precursors giving rise to background ESR signals, Can. J. Chem. 70 (1992) 2818–2827, https://doi.org/10.1139/v92-358.
[55] O. Welz, J.D. Savee, D.L. Osborn, S.S. Vasu, C.J. Percival, D.E. Shallcross, C.A. Taatjes, Direct kinetic measurements of Criegee intermediate (CH2OO) formed by reaction of CH2I with O2, Science 335 (2012) 204–207, https://doi.org/10.1126/science.1213229.
[56] Y. Tu, Z.X. Wang, Y. Shi, An efficient asymmetric epoxidation method for trans-olefins mediated by a fructose-derived ketone, J. Am. Chem. Soc. 118 (1996) 9806–9807, https://doi.org/10.1021/ja962345g.
[57] D. Yang, M.K. Wong, Y.C. Yip, Epoxidation of olefins using methyl (trifluoromethyl) dioxirane generated in situ, J. Org. Chem. 60 (1995) 3887–3889, https://doi.org/10.1021/jo00117a046.
[58] W. Adam, M. Müller, F. Prechtl, Dimethyldioxirane oxidation of titanium enolates: Diastereoselective α-hydroxylations, J. Org. Chem. 59 (1994) 2358–2364, https://doi.org/10.1021/jo00088a015.
[59] M.S. Kharasch, G. Sosnovsky, Structure of peroxides derived from cyclohexanone and hydrogen peroxide, J. Org. Chem. 23 (1958) 1322–1326, https://doi.org/10.1021/jo01103a021.
[60] J. Liu, Y. Yang, N. Liu, Y. Liu, H. Huang, Z. Kang, Total photocatalysis conversion from cyclohexane to cyclohexanone by C3N4/Au nanocomposites, Green Chem. 16 (2014) 4559–4565, https://doi.org/10.1039/C4GC01126K.
[61] A. Berkessel, T.J.S. Schubert, T.N. Müller, Hydrogenation without a transition-metal catalyst: on the mechanism of the base-catalyzed hydrogenation of ketones, J. Am. Chem. Soc. 124 (2002) 8693–8698, https://doi.org/10.1021/ja016152r.
[62] T. Ohkuma, M. Koizumi, J. Ikehira, T. Yokozawa, R. Noyori, Selective hydrogenation of benzophenones to benzhydrols. Asymmetric synthesis of unsymmetrical diarylmethanols, Org. Lett. 2 (2000) 659–662, https://doi.org/10.1021/ol9904139.
[63] J. Wu, J.-X. Ji, R. Guo, C.-H. Yeung, A.S.C. Chan, Chiral [RuCl2(dipyridylphosphane)(1,2-diamine)] catalysts: Applications in asymmetric hydrogenation of a wide range of simple ketones, Chem. Eur. J. 9 (2003) 2963–2968, https://doi.org/10.1002/chem.200204688.
[64] K. Hattori, H. Sajiki, K. Hirota, Chemoselective control of hydrogenation among aromatic carbonyl and benzyl alcohol derivatives using Pd/C (en) catalyst, Tetrahedron 57 (2001) 4817–4824, https://doi.org/10.1016/S0040-4020(01)00421-5.
[65] L.W. Gosser, D. Wilmington, Hydrogenation of a Diarylketone to a Diarylmethanol, US Patent 4302435, (1981).