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Selective One-step Aerobic Oxidation of Cyclohexane to ε-Caprolactone Mediated by *N*-hydroxyphthalimide (NHPI)

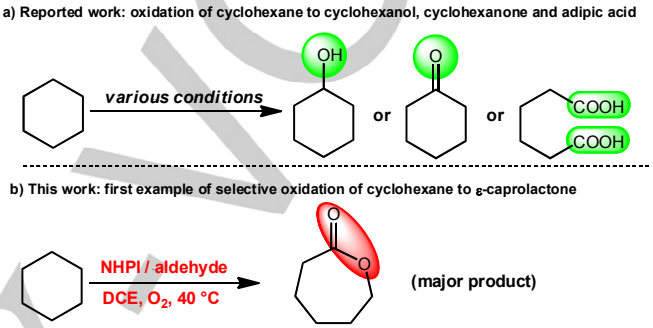
Lingyao Wang,[a] Yuanbin Zhang,[a] Renfeng Du,[a] Haoran Yuan,[a] Yongtao Wang,[a] Jia Yao,[a] and Haoran Li*[a, b]

Abstract: The selective one-step aerobic oxidation of cyclohexane to ε-caprolactone was achieved in the presence of *N*-hydroxyphthalimide (NHPI) and aldehyde under mild conditions. Remarkably, 12% of cyclohexane was converted with a selectivity of 77% of ε-caprolactone and 15% of KA oil. Control experiments indicated that NHPI accelerated the oxidation of aldehydes and peroxy radicals generated from aldehydes *in situ* were the key intermediates in the period of CH bond activation. 2,2,6,6-Tetramethylpiperidine 1-oxyl (TEMPO) addition and a series of *m*-chloroperoxybenzoic acid (*m*-CPBA) oxidation experiments showed that the oxidation proceeded *via* a complex radical chain mechanism.

The selective aerobic oxidation of hydrocarbons is one of the most important and challenging subjects in fundamental research and industrial production.[1] Cyclohexane as a raw material has been widely used for synthesis of KA oil (mixtures of cyclohexanone (CHONE) and cyclohexanol (CHOL) and adipic acid (AA), a well-known monomer of nylon polymers.[2] The approach of selective synthesis of CHOL, CHONE and AA by oxygenation of cyclohexane has been well studied for recent decades and a plenty of catalytic system have been reported including homogeneous and heterogeneous catalysts (Table S1).[3] ε-Caprolactone (ε-CL) is a precursor monomer for the production of polycaprolactone, which is known as a popular synthetic biodegradable polymer.[4] The current synthesis of ε-CL from cyclohexane undergoes two steps: 1) oxidation of cyclohexane to CHONE and 2) Baeyer-Villiger oxidation of CHONE to ε-CL.[5] Many efforts have been made to study these two separated reactions, but none has tried to realize the direct oxidation of cyclohexane to ε-CL. Considering the industrial cost as well as the synthetic economy, seeking out a one-step procedure for producing ε-CL from cyclohexane under mild conditions is of grand significance.

A common way of utilizing O_2 in transformation of hydrocarbons to oxygen-containing compounds is the addition of an aldehyde as a sacrificial agent (Mukaiyama conditions).[6] For example, Murahashi *et. al.* [6b, 7] found that the iron powder, copper salts, Ru-Co bi-metallic, Co(TPFPP) or Cu-crown ether could catalyze the oxidation of cyclohexane in the presence of acetaldehyde. Ishii and co-workers developed a series of catalyst systems combining *N*-hydroxyphthalimide (NHPI) and metal complexes to transform hydrocarbons.[3a, 8] Einhorn *et al.* [9] reported an aerobic oxidation of hydrocarbons to alcohols and ketones mediated by NHPI and acetaldehyde.

Herein, we would like to report an unprecedented facile method for selective and direct oxidation of cyclohexane into ε-CL. The reaction was mediated by NHPI with O_2 as the oxidant and aldehyde as the co-oxidation additive. (Scheme 1)



Scheme 1. Oxidation of cyclohexane.

The initial reaction was performed in 1,2-dichloroethane (DCE) at 30°C in the presence of 2 equivalents of benzaldehyde and 10 mol% of NHPI for 24 h. However, no ε-CL was generated (**Table 1**, entry 1). When the temperature rose to 35°C, the cyclohexane conversion increased to 4.8% with selectivity of 33.5% KA oil and 66.1% ε-CL (entry 2). At 40°C, the cyclohexane conversion was 12.3% with ε-CL selectivity of 77.3% and KA oil selectivity of 14.9% (entry 3). The continuous increase of temperature to 45°C or 50°C resulted in the loss of yields (entries 4, 5). Control experiments (Table 2, entries 1-2) indicated that no oxidation products were formed in the absence of benzaldehyde. And without NHPI, the sole benzaldehyde resulted a conversion of 1.9% without the generation of ε-CL (entry 3). Then, different solvents and aldehydes were examined. Other solvents such as MeCN, EtOAc and toluene were not effective as DCE (entries 4-7). In our previous report, we have explored the Baeyer-Villiger oxidation of CHONE promoted by substituted aromatic aldehydes and aliphatic aldehydes in detail. In this work, we chose 3-chloro-benzaldehyde, 4-fluoro-benzaldehyde, acetaldehyde, heptanal and isobutyraldehyde to study (entries 8-12). The results showed that 3-chloro-benzaldehyde and 4-fluoro-benzaldehyde were more efficient with ε-CL selectivity of 85 and 80% respectively while acetaldehyde, heptanal and isobutyraldehyde were less efficient but still provided ε-CL in 4, 16 and 8% selectivity respectively. Considering the lower commercial price of aliphatic aldehydes, it is meaningful that isobutyraldehyde and heptanal can serve as potential sacrificing agents in the oxidation reaction systems. Benzaldehyde as the sacrifice was also important to the reaction. Reducing or increasing the amount of benzaldehyde resulted in a small decrease of yields (Table S2, entries 1-6). The amount of NHPI was vital to the reaction. Varying the loading of NHPI to 15 or 20 mol% led to the lower yields of ε-CL (Table S2, entries 7-9).

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Table 1. Effect of different temperatures on the oxidatin of cyclohexane [a]

Entry	Temperature (°C)	Conv. (%) [b]	Selec.(%) [b]		
			CHOL	CHONE	ε-CL
1	30	1.0	61.1	34.7	0.0
2	35	4.8	6.5	27.0	61.1
3	40	12.3	5.6	9.3	77.3
4	45	9.7	8.0	14.3	70.9
5	50	8.3	10.2	16.0	67.0

[a] Reactions were conducted on a 2.0 mmol scale in 20 mL of DCE in a round bottom flask with an O_2 balloon for 24 h at 40 °C. [b] GC.

Table 2. Oxidation of cyclohexane in different solvents and aldehydes

Entry	Solvent	Aldehyde	Conv. (%) [b]	Select. (%)[b]		
				CHOL	CHONE	ε-CL
1	DCE	--	trace	0	0	0
2	DCE	--	trace	0	0	0
3[c]	DCE	PhCHO	1.9	30.9	59.4	0
4	DCE	PhCHO	12.3	5.6	9.3	77.3
5	MeCN	PhCHO	6.1	28.7	35.3	27.2
6	EtOAC	PhCHO	3.2	26.3	30.2	30.5
7	Toluene	PhCHO	0	0	0	0
8	DCE	3-Cl-PhCHO	15.0	2.1	3.3	85.4
9	DCE	4-F-PhCHO	14.3	6.3	7.1	80.4
10	DCE	CH_3CHO	3.5	46.0	23.0	11.8
11	DCE	$(CH_3)_3CHCHO$	6.6	24.6	54.8	15.8
12	DCE	n-C_6H_{13}-CHO	10.6	67.8	11.7	7.9

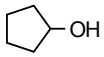
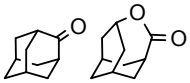
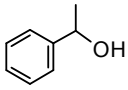
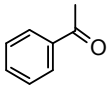
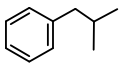
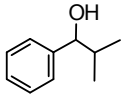
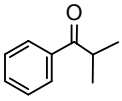
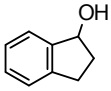
[a] Reactions were conducted on a 2.0 mmol scale in 20 mL of DCE in a round bottom flask with an O_2 balloon for 24 h at 40 °C. [b] GC. [c] in the absence of NHPI.

Table 3. Catalytic performance of NHPI and other reported catalyst system

Entry	Catalytic system	Conv. (%) [b]	Product (Selec.,%) [b]	Ref.
1	$Cu(OH)_2$ acetaldehyde (3 eq) CH_3CN	4.5	KA oil (96.0%)	7a
2	Fe/CH_3COOH heptanal (4 eq) DCM	11.0	KA oil (85.0%)	6b
3	NHPI acetaldehyde(1 eq) CH_3CN	8.0	KA oil (100%)	9
4	NHPI benzaldehyde (0.5 eq) DCE	5.7	KA oil (21.0%) ε-CL (76.3%)	This work
5	NHPI benzaldehyde(1 eq) DCE	7.5	KA oil (20.0%) ε-CL (77.2%)	This work
6	NHPI benzaldehyde(2 eq) DCE	12.3	KA oil (19.8%) ε-CL (77.3%)	This work

Table 3 demonstrated a comparison of reported catalysts and NHPI for the aerobic oxidation of cyclohexane. As it was shown, KA oil was the main product by previous catalytic system. In the presence of $Cu(OH)_2$ and 3 equivalents of acetaldehyde, 4.5% of cyclohexane was converted with 96% selectivity of KA oil.[7a] Fe/CH_3COOH catalytic system with 4 equivalents of heptanal, led to 11% conversion of cyclohexane and 85% selectivity of KA oil.[6b] Metal-free catalysts system, *eg*, NHPI, consumed 1 equivalent of acetaldehyde and resulted in a conversion of 8% with 100% KA oil selectivity for 72h.[9] In this work, we used NHPI as a metal-free catalyst with a loading of 0.5 to 2 equivalents of benzaldehyde in the solvent of DCE, and the cyclohexane conversion ranged from 5.7-12.3% with about 77% selectivity of ε-CL. Thus, NHPI/PhCHO/O_2/DCE is an efficient catalytic system for the direct oxidation of cyclohexane to ε-CL.

Table 4. NHPI/PhCHO-Promoted aerobic oxidation of various substrates.[a]

Entry	Substrate	Conv. (%) [b]	Product (Selec.,%) [b]		
1		12	 (6)	 (9)	 (77)
2		6	 (30)	 (26)	 (40)
3		30	 (89)	 (2)	 (2) (5)
4	n-C_8H_{18}	4	Octanol (40)		Octanone (56)
5		15	 (23)		 (68)
6		20	 (23)		 (68)
7		20	 (20)		 (72)

[a] Reactions were conducted on a 2.0 mmol scale in 20 mL of DCE in a round bottom flask with an O_2 balloon for 24 h at 40 °C. [b] GC.

The time curves of cyclohexane oxidation were shown in Figure 1(a). In this figure, we learned that both CHOL and CHONE selectivities in the reaction system decreased while ε-CL selectivity increased with the conversion of cyclohexane. These results indicated that ε-CL was easily produced from the *in-situ* formed CHONE by Baeyer-Villiger oxidation in the reaction system.[5f]

With the optimal reaction conditions in hand, we then tested the oxidation of other alkanes under the conditions. As shown in the Table 4, cycloalkanes were favorably transformed to the

corresponding lactones (entries 1-3). The oxidation of adamantane showed that the reactivity of C-H bonds were in the order tertiary > secondary > primary. However, poorly reactive linear alkanes and alkylated benzenes such as ethylbenzene, isobutylbenzene and indane were only converted to ketones and alcohols (entries 4-7).

To understand the solvent-induced radical effect, we investigated the intensity of free radicals generated by NHPI/PhCHO system in different solvents. Figure 1(b) showed that the PINO signal was very strong in DCE while no distinct PINO radicals formed in toluene, which were consistent with the results of the aerobic reaction oxidation in different solvents. Control experiments were conducted in the absence of benzaldehyde in different solvents (Figure S2). Moreover, trace amount of 1-chloroadamantane was detected as a side product by GC-MS in the reaction (SI, P11), which means DCE can partially dissociate to promote the propagation of radical chains. This result may account for the better performance of DCE compared to MeCN or toluene as radicals were more readily initiated.

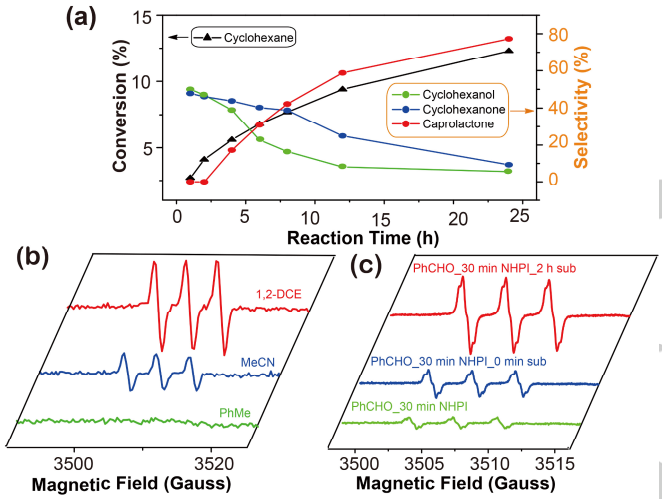


Figure 1. (a) The time curves of cyclohexane oxidation reaction. (b) EPR spectra of the mixture of NHPI and PhCHO in solvents of 1.2-DCE (red), MeCN (blue) and PhMe (green). (c) EPR spectra of the mixture of NHPI and PhCHO (green) with the addition of cyclohexane immediately (blue), and for 2 h (red).

The mechanistic aspects of the transformation were investigated by an additional experiment using a radical scavenger TEMPO (Table S3). No oxidation occurred in the presence of TEMPO, which confirmed the free radical-chain pathway of the reaction. When NHPI and 3-cholrobenzaldehyde were replaced by *m*-chloroperoxybenzoic acid (*m*-CPBA), only 0.5% conversion of cyclohexane was detected, which indicated that the active species involved in the oxidations was possibly the *in situ* formed acylperoxy radical instead of acylperoxyl acid (Table 5, entry 1).[9] After addition of NHPI into *m*-CPBA system, the conversion of cyclohexane and selectivity of ε-CL were improved (entries 2-5), suggesting that the oxidation proceeded *via* a complex radical chain mechanism. Moreover, the presence of O_2 could promote the conversion of KA oil to ε-CL. (entry 3, 4). Ingold and co-workers reported that the acylperoxy radicals derived from aldehydes are considerably more reactive in hydrogen atom abstraction from hydrocarbons than the peroxy radicals derived from the hydrocarbons.[10] The acylperoxy radial species and PINO lead to a hydrogen abstraction transfer via the homolytic cleavage of the sp^3 hybridized C–H bonds of the cyclohexane. Then cyclohexane radical reacted with acylperoxy radial to produce CHONE and CHOL, and then the CHONE was further oxidized to ε-CL under the same reaction conditions.

Some EPR experiments were carried out to detect the radicals involved in the reaction. When combining PhCHO and NHPI with air, a radical signal from PINO was detected (A = 4.56 G, g = 2.0069) (Figure 1(c), green curve). After the addition of cyclohexane to the solution, the PINO signal was immediately increased (blue curve). After reacting for 2 h, the PINO signal increased to a higher level (red curve). These indicated that the PINO was accumulated after addition of cyclohexane, probably due to the stabilization of PINO by cyclohexane in the radical chain propagation thus the PINO radical was increased.[11] The EPR spectrum of PINO induced by the UV light of NHPI was shown in Figure S1, which was consistent with the literature reported by Ishii.[12] In particular, Pedulli *et al.* [13] reported that PINO presented a triplet signal with a hyperfine coupling constant in *t*-BuOH of a_N=4.36 G. No EPR signals were observed in the blank experiments of PhCHO/O_2 or NHPI/O_2 system (Figure S3).

Table 5. Oxidatin of cyclohexane mediated by *m*-CPBA with NHPI [a]

Entry	NHPI amount (%)	Conv. (%) [b]	Select.(%) [b]		
			CHOL	CHONE	ε-CL
1	0	0.5	0	32.6	42.7
2	10	2.0	14.6	32.4	29.1
3	100	4.2	11.5	10.9	70.3
4[c]	100	4.2	20.2	14.8	55.5
5	200	12.0	10.4	4.7	84.8
6[d]	10	trace	0	0	0

[a] Reactions were conducted at 2.0 mmol scale with 20 mL of DCE in a round bottom flask with 1 eq. *m*-CPBA for 24 h at 40 °C in the presence of O_2. [b] GC. [c] In the absence of O_2. [d] In the absence of *m*-CPBA.

In conclusion, we have developed the first one-step process for the aerobic oxidation of cyclohexane to ε-CL. The reaction was carried out under mild conditions and promoted by a mixture of NHPI and PhCHO without transition metals. This catalytic system is able to activate the cyclohexane ring at relatively low temperature and under low pressure of air. Mechanistically, a radical-chain pathway was conjectured. Our work not only provides an economic strategy for the synthesis of industrially important ε-CL, but also indicates the great potential of NHPI/aldehyde/O_2 catalytic oxidation system that can be possibly utilized in other oxidation reactions. Further studies will focus on the reaction mechanism and the improvement of the process for the industrial applications and expansion of the novel method to other systems.

Experimental Section

Materials. Cyclohexane (>99.0%), cyclohexanone (>99.0%), cyclohexanol (>99.0%), adamantane (99.5%), 1-adamantanol (98%), 2-adamantanol (98%), 2-adamantanone (99%), cyclopentane (99%), *tert*-butyl acetate (>99.0%) and were purchased from TCI without further purification unless indicated. 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) (98%), *N*- hydroxyphthalimide (NHPI) (98%), biphenyl (99.5%), benzaldehyde (98%) and ε-caprolactone (99.5%) were purchased from J & K Scientific Ltd. without further purification unless indicated. Acetonitrile, toluene, ethyl acetate were analytical grade and purchased from J & K Scientific Ltd. 1,2-Dichloroethane (DCE) (99.5%), 3-chlorobenzaldehyde (98%), 4-fluorobenzaldehyde, cyclopentanol (99%), delta-valerolactone (98%), cyclopentanone (99%) and isobutyraldehyde (98%) were purchased from Energy Chemical without further purification unless indicated. Heptanal (98%) and 3-chloroperoxybenzoic acid (85%) were purchased from Tansoole without further purification. Other chemicals were purchased from Adamas-beta without further purification.

General Methods. The progress of the reaction was monitored by taking samples at various intervals to be analyzed using gas chromatograph (GC) (Agilent 7820A) equipped with a DB-35/ZB-35/HP-35 column (30 m × 0.32 mm × 0.25 mm) and a Flame Ionization Detector (FID). The conversion was calculated on the basis of the peak area ratio of ketones against the internal standard, biphenyl. The product yields were calculated on the basis of the peak area ratio of lactones or esters against the internal standard. The structural analysis of target product was conducted on a Gas chromatography/ Mass spectrometry (GC/MS) (Agilent 7200-Q-TOF). EPR spectra were obtained by using a computer controlled X-band (9.5GHz) EPR spectrometer (Bruker A300).

General Procedure for Cyclohexane Oxidation (a) with oxygen In a typical reaction, cyclohexane (2 mmol), benzaldehyde (4 mmol), NHPI (10 mol%) and 1,2-dichloroethane (20 mL) were placed into a three-necked round bottom flask (50 mL) equipped with an oxygen balloon and a magnetic stir bar. The mixture was stirred at 40 ºC for 24 hours. The reaction was monitored by a GC instrument. The conversion was calculated on the basis of the peak area ratio of cyclohexane against the internal standard, biphenyl. The product yields were calculated on the basis of the peak area ratio of cyclohexanol, cyclohexanone, and ε-caprolactone against the internal standard. **(b) with *m*-CPBA** In a typical reaction, cyclohexane (2 mmol), *m*-CPBA (4 mmol), NHPI (10 mol%) and 1,2-dichloroethane (20 mL) were placed into a three-necked round bottom flask (50 mL) equipped with an oxygen balloon and a magnetic stir bar. The mixture was stirred at 40°C for 24 hours. The reaction was monitored by GC instrument. The conversion was calculated on the basis of the peak area ratio of cyclohexane against the internal standard, biphenyl. The product yields were calculated on the basis of the peak area ratio of cyclohexanol, cyclohexanone, and ε-caprolactone against the internal standard. Control experiment was conducted in the absence of NHPI.

General EPR experiments in different solvents. To a 25 mL schlenk tube with a magnetic stirrer was added 0.2122 g (2 mmol) of benzaldehyde, 0.0163 g (0.1 mmol) of NHPI and 10 mL of 1, 2-dichloroethane (DCE). The mixture was stirred at 40 ºC for 30 min at atmospheric pressure. Thereafter, EPR was measured immediately. The EPR spectra of the reaction solution were obtained by using a computer controlled X-band (9.5 GHz) EPR spectrometer (Bruker A300). The solvent DCE was replaced by CH_3CN and Toluene. Control experiments were conducted in the absence of bezaldehyde in different solvents.

General EPR experiments with NHPI To a 50 mL three-necked glass flask fitted with a water cooled reflux condenser, a magnetic stir bar and an oxygen balloon was added 0.4245 g (4 mmol) of benzaldehyde and 20 mL of 1,2-dichloroethane (DCE). The mixture was stirred at 40°C for 30 min at atmospheric pressure. Then 0.0326 g (0.2 mmol) of NHPI was added into the mixture and the mixture was stirred for another 30 min. The EPR spectra of the reaction solution (Figure 1(c), green) were obtained by using a computer controlled X-band (9.5GHz) EPR spectrometer (Bruker A300). Thereafter, EPR was measured immediately upon addition of 0.168 g (2 mmol) of cyclohexane into the reaction system (blue). The reaction was continued for 2 h before measuring EPR (red).

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Keywords: cyclohexane oxidation• ε-caprolactone • one-step • NHPI • metal-free

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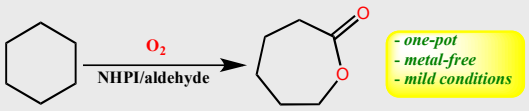

direct aerobic oxidation of cyclohexane to ε-caprolactone

The selective one-step aerobic oxidation of cyclohexane to ε-caprolactone was achieved in the presence of *N*-hydroxyphthalimide (NHPI) and aldehyde under mild conditions with 12% conversion of cyclohexane and a selectivity of 77% of ε-caprolactone and 15% of KA oil.

*Lingyao Wang, Yuanbin Zhang, Renfeng Du, Haoran Yuan, Yongtao Wang, Prof. Jia Yao, Prof. Haoran Li**

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