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Aerobic Oxidation of Cyclohexane using *N*-Hydroxyphthalimide Bearing Fluoroalkyl Chains

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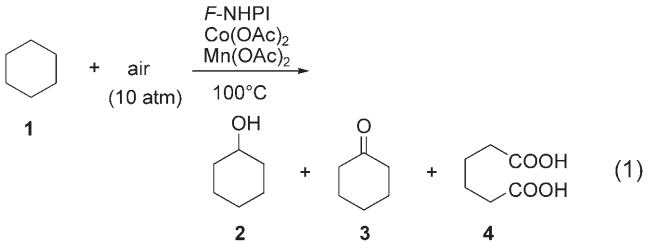
Abstract: The *N*-hydroxyphthalimide derivatives, F_{15}- and F_{17}-NHPI, bearing a long fluorinated alkyl chain, were prepared and their catalytic performances were compared with that of the parent compound, *N*-hydroxyphthalimide (NHPI). The oxidation of cyclohexane under 10 atm of air in the presence of fluorinated F_{15}- or F_{17}-NHPI, cobalt diacetate [$Co(OAc)_2$], and manganese diacetate [$Mn(OAc)_2$] without any solvent at 100 °C afforded a mixture of cyclohexanol and cyclohexanone (K/A oil) as major products along with a small amount of adipic acid. It was found that F_{15}- and F_{17}-NHPI exhibit higher catalytic activity than NHPI for the oxidation of cyclohexane without a solvent. However, for the oxidation in acetic acid all of these catalysts afforded adipic acid as a major product in good yield and the catalytic activity of NHPI in acetic acid was almost the same as those of F_{15}- and F_{17}-NHPI. The oxidation by F_{15}- and F_{17}-NHPI catalysts in trifluorotoluene afforded K/A oil in high selectivity with little formation of adipic acid, while NHPI was a poor catalyst under these conditions, forming K/A oil as well as adipic acid in very low yields. The oxidation in trifluorotoluene by F_{15}- and F_{17}-NHPI catalysts was considerably accelerated by the addition of a small amount of zirconium(IV) acetylacetonate [$Zr(acac)_4$] to the present catalytic system to afford selectively K/A oil, but no such effect was observed in the NHPI-catalyzed oxidation in trifluorotoluene.

Keywords: aerobic oxidation; cyclohexane; fluorinated *N*-hydroxyphthalimide; K/A oil

Introduction

The aerobic oxidation of cyclohexane (**1**) is a very important industrial process for the production of primary and specialty chemicals like cyclohexanol (**2**), cyclohexanone (**3**), and adipic acid (**4**).[1] Nowadays, the aerobic oxidation of **1** leading to a mixture of **2** and **3** which is generally referred to as K/A oil is usually carried out under the influence of a small amount of cobalt salts. In the conventional autoxidation of **1** using cobalt catalysts, however, the reaction calls for operation at around 150 °C.[2] Under these conditions, the oxidation results in cleaved products like glutaric acid and maleic acid as well as undesired decarboxylated side products. Therefore, the oxidation is usually operated in lower conversion (3–5%) of **1** to keep the selectivity to K/A oil. If the aerobic oxidation of **1** is able to run at a lower temperature of around 100 °C, it is possible to carry out the reaction at higher conversion of **1**. Fortunately, we have recently developed a novel catalytic system consisting of *N*-hydroxyphthalimide (NHPI) combined with Co(II) for the aerobic oxidation of saturated hydrocarbons which is generally referred to as the Ishii oxidation system.[3] By the use of our catalytic system, cycloalkanes can be oxidized in acetic acid even at 100 °C to give oxygenated products like alcohols, ketones and dicarboxylic acids in higher conversions.[4] However, the NHPI-catalyzed aerobic oxidation of cycloalkanes like **1** without a solvent was difficult to perform in higher conversion because of the slight solubility of NHPI bearing a hydroxyimide (>N-OH) group in hydrophobic media like cycloalkane **1**. Thus, we prepared lipophilic NHPI derivatives having long alkyl chains which are easily dissolved in hydrocarbons like **1**, and the aerobic oxidation of **1** without a solvent by these lipophilic NHPI catalysts was found to give cyclohexanol **2** and cyclohexanone **3** along with a small amount of adipic acid **4** in higher conversion compared with the oxidation by NHPI.[5] In continuation of our study to improve the catalytic performance of NHPI for the aerobic oxidation of **1**, we prepared two different

types of fluorinated *N*-hydroxyphthalimide derivatives (*F*-NHPI), F_{15}-NHPI and F_{17}-NHPI, and the catalytic performances of these *F*-NHPI derivatives were compared with that of the parent NHPI catalyst [Eq.(1)].

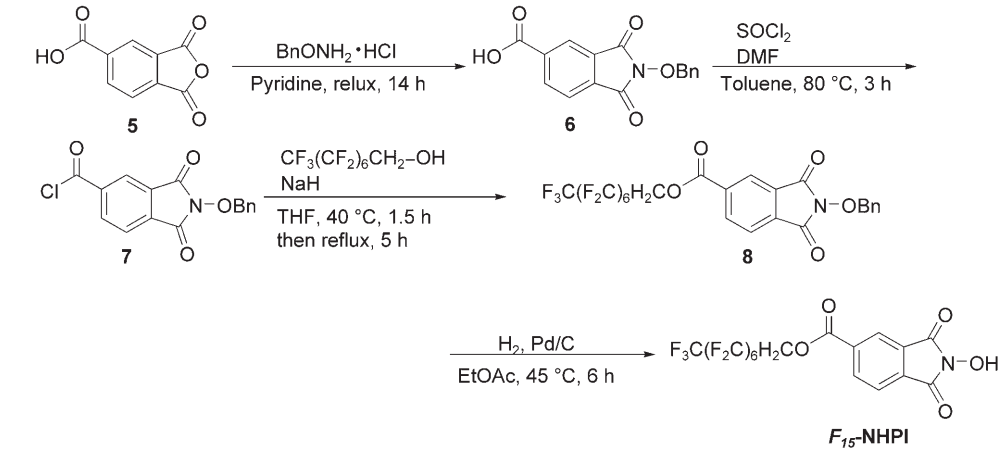


Results and Discussion

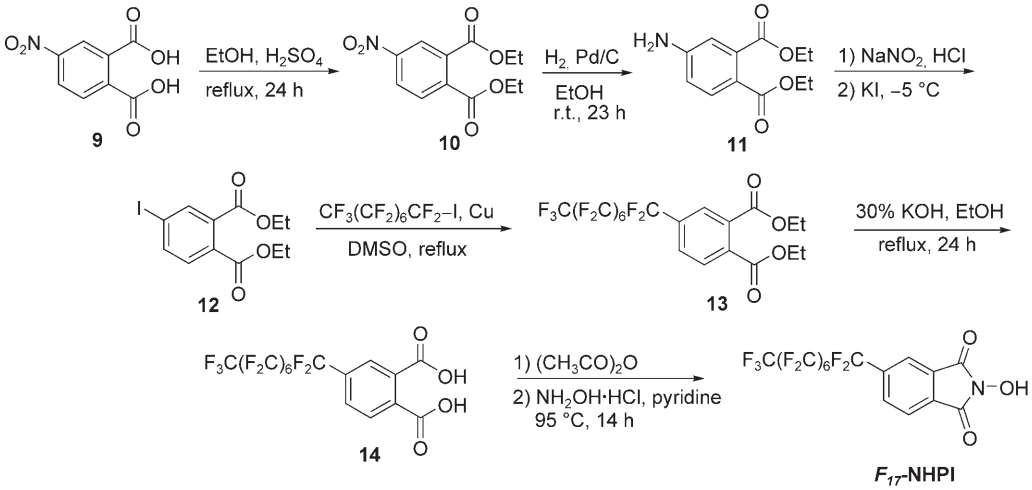
The fluorinated *N*-hydroxyphthalimide catalysts, F_{15}- and F_{17}-NHPI, were prepared according to Scheme 1 and Scheme 2. The reaction of commercially available trimellitic anhydride (**5**) with *O*-benzylhydroxylamine hydrochloride afforded *N*-benzyloxyphthalimide-4-carboxylic acid (**6**). Treatment of **6** with $SOCl_2$ followed by introduction of the fluorinated substituent led to **8** which, on subsequent hydrogenation over Pd/C, resulted in F_{15}-NHPI in a total yield of 28% (Scheme 1). On the other hand, F_{17}-NHPI was prepared from 4-nitrophthalic acid (**9**) through a 6-step reaction involving Sandmeyer iodination and a Cu-catalyzed coupling reaction with fluorinated alkyl iodide as the key reactions (Scheme 2).

In order to evaluate the catalytic performances of the fluorinated *N*-hydroxyphthalimide derivatives (*F*-NHPI), the aerobic oxidation of **1** by F_{15}- and F_{17}-NHPI catalysts was examined and compared with that by the parent NHPI catalyst (Table 1).

The aerobic oxidation of **1** (4 mL, *ca.* 37 mmol) was carried out under air (10 atm) in the presence of NHPI (25 μmol), $Co(OAc)_2{\cdot}4H_2O$ (20 μmol), and $Mn(OAc)_2{\cdot}4H_2O$ (10 μmol) without any solvent at



Scheme 1. Preparation of F_{15}-NHPI.



Scheme 2. Preparation of F_{17}-NHPI.

Table 1. Solvent-free aerobic oxidation of cyclohexane(**1**) using *N*-hydroxyphthalimide derivatives.[a]

Entry	Catalyst	Time [h]	Yield [%][b]			Ratio	TON[c]
			2	**3**	**4**	**2/3**	
1	NHPI	6	622	468	trace	1.32	10.9
2	NHPI	14	1060	836	5	1.27	19.0
3	F_{15}-NHPI	6	1200	809	18	1.48	20.3
4	F_{15}-NHPI	14	1712	2035	29	0.84	37.8
5	F_{17}-NHPI	6	1278	1485	21	0.86	27.8
6	F_{17}-NHPI	14	2108	2424	32	0.87	45.6

[a] Compound **1** (37 mmol) was allowed to react under air (10 atm) at 100 °C in the presence of NHPI or *F*-NHPI (25 μmol), $Co(OAc)_2{\cdot}4H_2O$ (20 μmol), $Mn(OAc)_2{\cdot}4H_2O$ (10 μmol).
[b] GC yield based on the catalyst used.
[c] TON = **2**+**3**+**4** (mmol)/NHPI(or *F*-NHPI) (mmol).

100 °C for 6 h or 14 h. The oxidation of **1** by NHPI for 6 h led to **2** (622%), **3** (468%) and a trace amount of **4** and the total turnover number (TON) of the NHPI was 10.9 (entry 1). The yields and turnover number (TON) were based on the catalyst used. When the reaction time was prolonged to 14 h, the yields of **2**, **3**, and **4** were increased to 1060%, 836% and 5%, respectively, and the TON attained was 19 (entry 2). Under these conditions, adipic acid **4** was scarcely formed by NHPI (entries 1 and 2). In contrast to the poor solubility of NHPI in hydrocarbon **1**, the *F*-NHPI catalysts were readily dissolved in cyclohexane **1**. F_{15}-NHPI catalyst gave **2** (1200%), **3** (809%), and **4** (18%) in a TON of 20.3 after 6 h (entry 3), and **2** (1712%), **3** (2035%), and **4** (29%) in a TON of 37.8 after 14 h (entry 4). Similarly, the oxidation by F_{17}-NHPI catalyst afforded **2** (1278%), **3** (1485%), and **4** (21%) in a TON of 27.8 after 6 h (entry 5), and **2** (2108%), **3** (2424%) and **4** (32%) in a TON of 45.6 after 14 h (entry 6). These results show that fluorinated catalysts (*F*-NHPI) were considerably more active than NHPI for the aerobic oxidation of **1**. Among the three catalysts examined, the F_{17}-NHPI catalyst involving a long fluoroalkyl chain was found to be the most active. The higher activity of F_{15}- and F_{17}-NHPI compared to NHPI may be attributed to the improved solubility of the *F*-NHPI catalysts in **1** and the activation of *N*-hydroxyphthalimide groups by the introduction of fluorinated substituents having a strong electron-withdrawing effect. In general, electron-withdrawing substituents on substituted *N*-hydroxyphthalimides are known to accelerate the oxidation of hydrocarbons.[6] Thus, it was found that the catalytic activity of NHPI was increased by improving the solubility in **1** and by introducing an electron-withdrawing substituent like a fluoroalkyl group. We confirmed that no oxidation reaction took place in the absence of NHPI.

Since there have been several reports on the acceleration effect of Zr species for the aerobic oxidation of alkylaromatic hydrocarbons like *p*-xylene over Co catalysts,[7] the effect of Zr species for the aerobic oxidation of **1** by the NHPI/$Co(OAc)_2$/$Mn(OAc)_2$ system was examined. The results are summarized in Table 2.

By the addition of $Zr(acac)_4$ (10 μmol) to the NHPI/$Co(OAc)_2$/$Mn(OAc)_2$ system, **1** was converted to **2** (856%), **3** (794%), and **4** (12%) after 6 h and to **2** (1796%), **3** (1962%), and **4** (48%) after 14 h, and the TONs of the NHPI oxidation of **1** were increased from 10.9 at 6 h and 19.0 at 14 h in the absence of $Zr(acac)_4$ to 16.6 at 6 h and 38.1 at 14 h in the presence of $Zr(acac)_4$, respectively (entries 1 and 2). Similarly, the TONs of F_{15}-NHPI after adding $Zr(acac)_4$ were increased from 20.3 to 35.7 at 6 h and from 37.8 to 49.2 at 14 h (entries 3 and 4). The formation of adipic acid **4** was also increased from 29% to 160% upon adding $Zr(acac)_4$ (entry 4 in Table 1 and Table 2). The considerable accelerating effect of $Zr(acac)_4$ was observed in the oxidation by F_{17}-NHPI, and the TON for F_{17}-NHPI at 14 h was 56.9. In particular, a remarkable increase of the yield of adipic acid **4** (308%) was observed compared with the yield of **4** (32%) in the absence of $Zr(acac)_4$ (entry 6 in Table 1 and Table 2).

Table 2. Effect of $Zr(acac)_4$ on solvent-free aerobic oxidation of cyclohexane (**1**).[a]

Entry	Catalyst	Time [h]	Yield [%][b]			Ratio	TON[c]
			2	**3**	**4**	**2/3**	
1	NHPI	6	856	794	12	1.08	16.6
2	NHPI	14	1796	1962	48	0.92	38.1
3	F_{15}-NHPI	6	1608	1904	56	0.84	35.7
4	F_{15}-NHPI	14	1940	2820	160	0.69	49.2
5	F_{17}-NHPI	6	1604	2348	52	0.68	40.0
6	F_{17}-NHPI	14	2280	3104	308	0.73	56.9

[a] Compound **1** (37 mmol) was allowed to react under air (10 atm) at 100 °C in the presence of NHPI or *F*-NHPI (25 μmol), $Co(OAc)_2{\cdot}4H_2O$ (20 μmol), $Mn(OAc)_2{\cdot}4H_2O$ (10 μmol), and $Zr(acac)_4$ (10 μmol).
[b] GC yield based on the catalyst used.
[c] TON = **2**+**3**+**4** (mmol)/NHPI (or *F*-NHPI) (mmol).

Table 3. Aerobic oxidation of cyclohexane (**1**) in acetic acid or TFT.[a]

Entry	Catalyst	Solvent	Yield [%][b,c]			Ratio[c]	TON[c,d]
			2	**3**	**4**	**2/3**	
1	NHPI	AcOH	2096 (1824)	604 (260)	5000 (4720)	3.47 (7.02)	77.0 (68.0)
2	F_{15}-NHPI	AcOH	2484 (2516)	1044 (400)	5108 (5280)	2.38 (6.29)	86.4 (82.0)
3	F_{17}-NHPI	AcOH	2596 (2536)	1152 (408)	5120 (5320)	2.25 (6.22)	88.7 (82.6)
4	NHPI	TFT[e]	1144 (828)	1076 (912)	trace (trace)	1.06 (0.91)	22.2 (17.4)
5	F_{15}-NHPI	TFT[e]	2996(1456)	4800 (1052)	120 (12)	0.62 (1.38)	79.2 (25.2)
6	F_{17}-NHPI	TFT[e]	3556 (1772)	5484 (1504)	196 (36)	0.65 (1.18)	92.4 (33.1)

[a] Compound **1** (37 mmol) was allowed to react in the solvent (4 mL) at 100 °C for 6 h in the presence of NHPI or *F*-NHPI (25 μmol), $Co(OAc)_2{\cdot}4H_2O$ (20 μmol), $Mn(OAc)_2{\cdot}4H_2O$ (10 μmol), and $Zr(acac)_4$ (10 μmol).
[b] GC yield based on the catalyst used.
[c] The numbers in parentheses show yields in the reaction without $Zr(acac)_4$.
[d] TON = **2** + **3** + **4** (mmol)/NHPI(or *F*-NHPI) (mmol).
[e] TFT = trifluorotoluene.

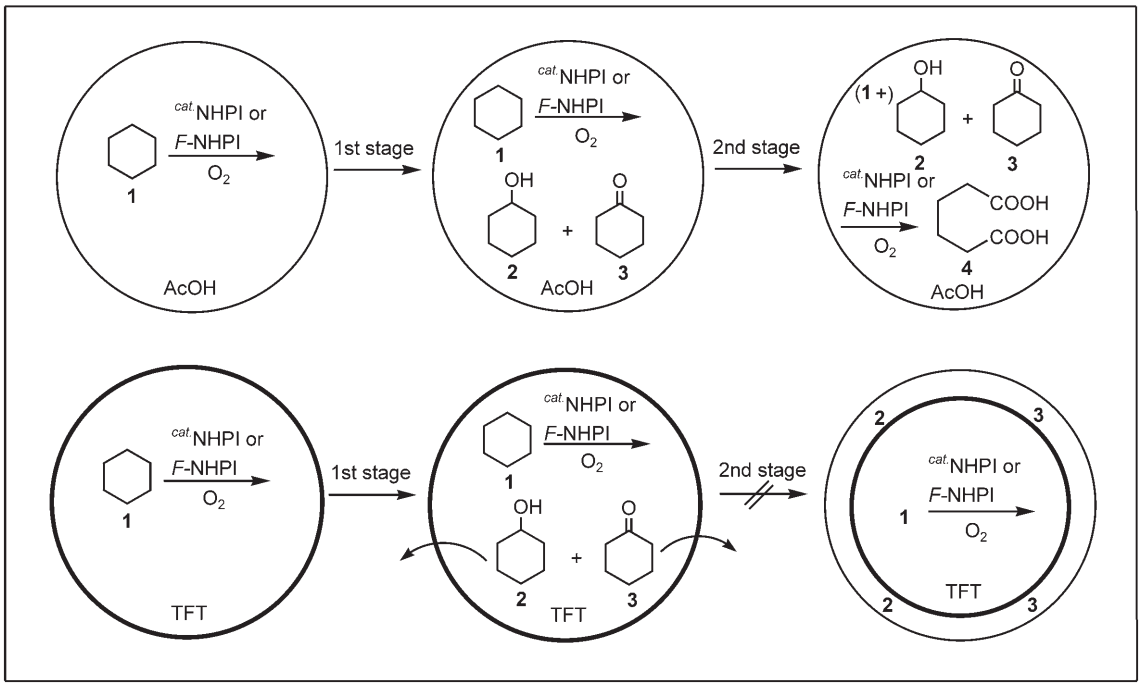
Partenheimer describes that the accelerating effect of Zr species on the Co/Mn/Br-catalyzed aerobic oxidation of *p*-xylene is a result of the strong Lewis acidity of Zr(IV) species that promotes the decomposition of benzyl hydroperoxide to benzaldehyde and water as well as of the formation of a polynuclear Co/Mn/Zr coordination compound.[6] In the present work, the effect of Zr species on the aerobic oxidation of **1** by NHPI and *F*-NHPI derivatives seems to be similar to those pointed out by Partenheimer for the aerobic oxidation of alkylaromatic hydrocarbons, but it needs more detailed study to reveal the actual effect of the Zr species on the present oxidation.

In order to probe the influence of the polarity of solvents, we next examined the oxidation of **1** by NHPI and *F*-NHPI catalysts in acetic acid (Table 3). As expected, NHPI is readily dissolved in acetic acid and **1** was smoothly oxidized to give **2** (1824%), **3** (260%), and **4** (4720%) in higher yields as compared with the oxidation of **1** without solvent. The TON of the NHPI oxidation was considerably increased from 10.9 without solvent (entry 1 in Table 1) to 68 in acetic acid (entry 1). It is noteworthy that adipic acid **4** was obtained as a major product in preference to **2** and **3** (entry 1). A similar tendency was also observed in the oxidations by F_{15}- and F_{17}-NHPI catalysts in acetic acid (entries 2 and 3). The TON for the oxidation of **1** by F_{17}-NHPI in acetic acid was 82.6 (entry 3). The fact that the ratio of **2** to **3** in acetic acid was approximately 6 to7 indicates that cyclohexanone **3** was oxidized in preference to **2** to give adipic acid **4**.

It is very attractive to compare the aerobic oxidation of **1** by NHPI with that by the *F*-NHPI catalysts in several solvents under the same reaction conditions (Table 3). The oxidation of **1** by NHPI in trifluorotoluene (TFT) was found to be accelerated to some extent compared with that in the absence of solvent, and the TON of the reaction was increased from 16.6 without solvent (entry 1 in Table 2) to 22.2 in TFT (entry 4 in Table 3). However, the TON (22.2) in TFT was very low compared with the TON (77.0) in acetic acid. This is believed to be due to the lower solubility of NHPI in TFT than that in acetic acid. In contrast, the oxidation of **1** by F_{15}- and F_{17}-NHPI catalysts in TFT led to high TONs for F_{15}-NHPI (79.2) and for F_{17}-NHPI (92.4) (entries 5 and 6). Furthermore, these TONs for the F_{15}- and F_{17}-NHPI catalysts in TFT were similar to those in acetic acid, probably because both catalysts can be readily dissolved in TFT solvent. Another important feature of the oxidation by *F*-NHPI catalysts in TFT is that the formation of adipic acid **4** was markedly suppressed in TFT compared with acetic acid (entries 2, 3, 5, and 6). These results suggest that the solvent used is a crucial factor to determine the product selectivity and the catalyst performance for the oxidation of **1**. It is interesting to note that there is no considerable addition effect of $Zr(acac)_4$ on the NHPI catalyst system in the oxidation of **1** in TFT (entry 4), while a remarkable acceleration effect of $Zr(acac)_4$ was observed in the oxidation by *F*-NHPI in TFT (entries 5 and 6).

The features of the oxidation of **1** by NHPI and *F*-NHPI in acetic acid and TFT may be illustrated as shown below (Scheme 3).

In the case of the aerobic oxidation using acetic acid as a solvent, NHPI and *F*-NHPI as well as substrate **1** are easily dissolved in acetic acid, and the oxidation of **1** is thought to proceed smoothly to give cyclohexanol **2** and cyclohexanone **3** (1st stage). Since the resulting **2** and **3**, which are also easily dissolved in the solvent, are more reactive than cycloalkane **1**, they are further oxidized with ease to give adipic acid **4** as a main product (2nd stage). In the oxidation in acetic acid, all of the compounds involving NHPI and *F*-NHPI catalysts used are readily dissolved in acetic acid, and then **1** as well as the resulting products **2** and **3** would be smoothly oxidized by both catalysts to give adipic acid **4** in a similar extent. Therefore, there seems to be no considerable difference in the



Scheme 3. Illustration of the selectivity for the aerobic oxidation of **1** in AcOH and TFT.

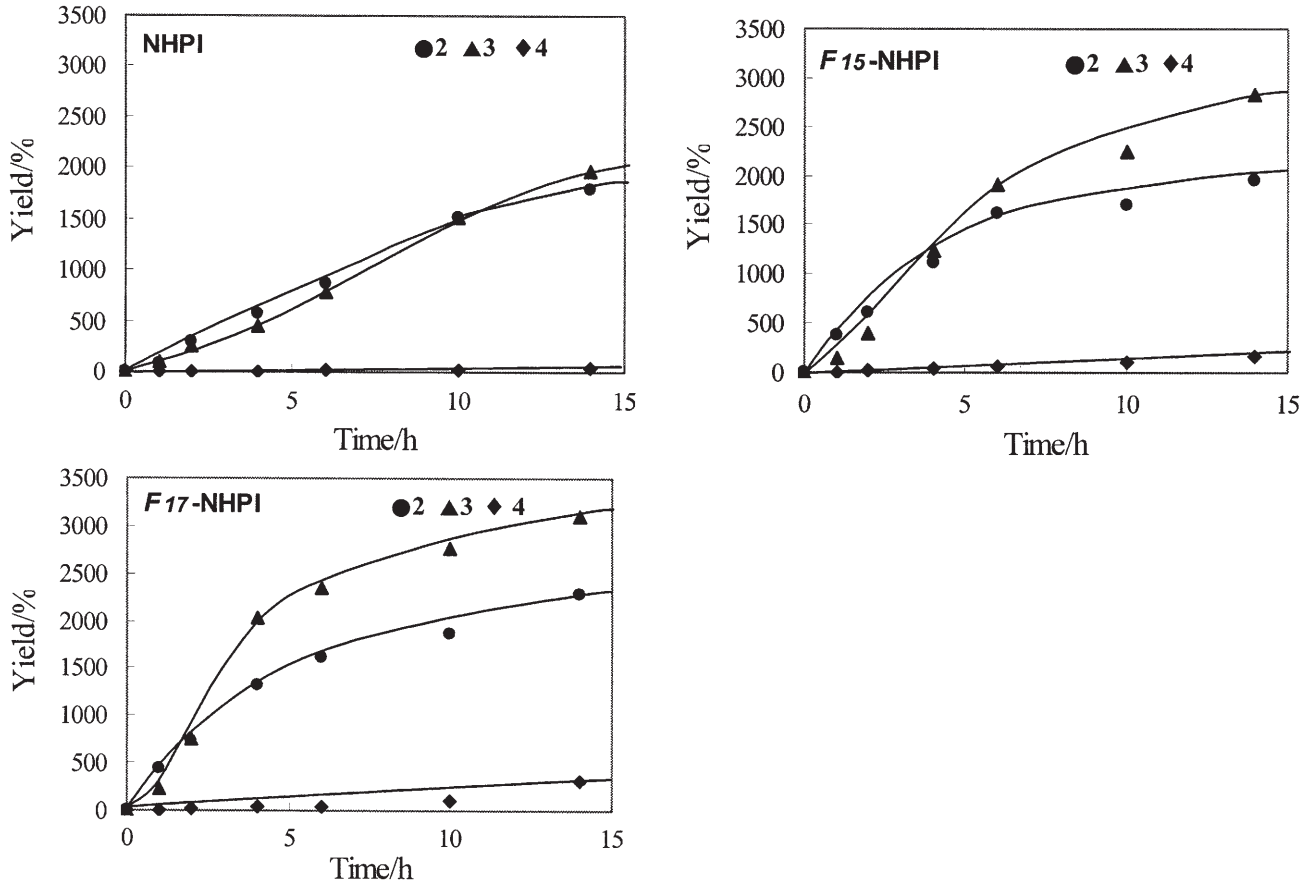


Figure 1. Time-conversion curves of the aerobic oxidation of **1** with NHPI, F_{15}-NHPI, and F_{17}-NHPI catalyst system. Reaction conditions were the same as entry 2 (for NHPI), entry 4 (for F_{15}-NHPI), and entry 6 (for F_{17}-NHPI) in Table 2.

catalytic performance of the NHPI and *F*-NHPI for the oxidation of **1**. On the other hand, in the oxidation of **1** by *F*-NHPI in TFT, since both *F*-NHPI and **1** can be readily dissolved in TFT, **1** would be oxidized to **2** and **3** (1st stage). However, it is thought that the generated **2** and **3** may be excluded to the outer sphere of TFT, because they, in particular **2**, are difficult to be dissolved in TFT. In fact, a mixture of **2** and TFT gave a cloudy solution. As a result, the oxidation of the 2nd stage by *F*-NHPI in TFT may be negligibly small. Therefore, the oxidation of **1** by *F*-NHPI in TFT is thought to lead to **2** and **3** in high selectivity with little formation of **4**.

The highest TON (92.4) was obtained in the oxidation by F_{17}-NHPI in TFT rather than acetic acid (entry 6). Therefore, the oxidation of **1** by fluorinated NHPI catalysts in TFT would provide to an attractive selective route to the K/A oil, in particular to **3**. These results show that fluorinated groups, possessing strong electron-withdrawing character and lipophilicity play dual functions, i.e., the activation of the *N*-hydroxyphthalimide group and increasing of the solubility in **1** and TFT of the catalyst.

Figure 1 shows the time-conversion curves of the aerobic oxidation of **1** by the three catalytic systems.

In the oxidation by the NHPI/Mn(II)/Co(II)/Zr(IV), the yields of **2** and **3** were linearly increased with time and the ratio of **2** to **3** was close to unity during the oxidation. On the other hand, in the oxidation by the F_{15}- and F_{17}-NHPI/Mn(II)/Co(II)/Zr(IV) systems, **2** and **3** were rapidly formed up to 6 h, but the rate of formation rate of these products became slower as time proceeded, which is probably due to degradation of the catalyst.

Conclusions

We have prepared *N*-hydroxyphthalimide derivatives (F_{15}- and F_{17}-NHPI) bearing a long fluorinated alkyl chain. The F_{15}- and F_{17}-NHPI catalysts efficiently promoted the aerobic oxidation of cyclohexane **1**. The oxidation by F_{15}- and F_{17}-NHPI catalysts in TFT provides a useful synthetic method for K/A oil from cyclohexane **1** under mild conditions.

Experimental Section

General Methods

The starting materials are commercially available and used without further purification. GC analysis was performed with a flame ionization detector using a 0.2 mm × 30 mm capillary column (OV-17). ^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra were measured in $CDCl_3$, CD_3OD, or acetone-d_6 with Me_4Si or $CFCl_3$ (for ^{19}F) as the internal standard. Infrared (IR) spectra were measured using KBr pellets. Mass spectra were obtained at an ionization energy of 70 eV. The yields of products were estimated from the peak areas on the basis of the internal standard technique by the use of GC.

General Procedure for the Oxidation of Cyclohexane (1) under Air

Cyclohexane (4 mL, *ca.* 37 mmol), NHPI derivatives (25 μmol), $Co(OAc)_2$ and $Mn(OAc)_2$ were placed in a 50-mL Teflon-coated autoclave, and 10 atm of air was charged. After stirring at 100 °C for 6 h, the mixture was cooled to room temperature, diluted with ethanol, and GC analysis was performed to determine the amount of cyclohexanol, cyclohexanone, and the unreacted cyclohexane. After removal of the solvent under reduced pressure, a catalytic amount of concentrated sulfuric acid and ethanol (10 mL) were added to the resulting mixture, and the solution was stirred at 100 °C for 15 h. The resulting solution was cooled to room temperature, and GC analysis was performed to determine the yield of adipic acid.

Preparation of (2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-Pentadecafluoro)-octyl *N*-Benzyloxyphthalimide-4-carboxylate (8)

To a solution of *O*-benzylhydroxylamine hydrochloride (1.60 g, 10 mmol) in pyridine (32 mL) was added trimellitic anhydride (**5**) (1.92 g, 10 mmol) slowly at room temperature. When all the trimellitic anhydride had dissolved in the solution, the reaction mixture was refluxed for 14 h. Then it was cooled to room temperature, and acidified with 4 M HCl solution. The organic substances were extracted with EtOAc (60 mL × 3), followed by washing with 1 M HCl solution, and dried over Na_2SO_4. After evaporating the solvent at reduced pressure, the crude *N*-benzyloxythalimide-4-carboxylic acid (**6**) was obtained; yield: 2.7 g (9.09 mmol).

Then compound **6** was dissolved in toluene (50 mL), and thionyl chloride (3.98 mL, 54.54 mmol) and a catalytic amount of DMF (0.1 mL) were added to the mixture at room temperature. The reaction mixture was stirred at 80 °C for 3 h. Then it was cooled to room temperature, and the excess thionyl chloride and toluene was evaporated by distillation under reduced pressure. The resulting residue was washed with hexane (10 mL × 3), and dried under vacuum to afford **7**.

Then, to a suspension of NaH (0.33 g, 8.25 mmol, *ca.* 60%) in THF (20 mL) was added a solution of 2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-pentadecafluoro-1-octanol (3.3 g, 8.25 mmol) in THF (10 mL) at room temperature under argon atmosphere. After stirring 15 min at 40 °C, the solution of **7** (2.6 g, 8.25 mmol) in THF (30 mL) was added to the reaction mixture. After stirring for 1.5 h at 40 °C and at reflux for 5 h, the mixture was cooled to room temperature, acidified with 1 M HCl solution, and Et_2O (80 mL) was added. The organic layer was separated and dried over Na_2SO_4. After evaporating the solvent at reduced pressure, the crude product was purified by silica gel column chromatography (*n*-hexane/EtOAc = 5/1) to afford **8** in a pure form; yield: 2.31 g (34% over 3 steps). ^{1}H NMR (270 MHz, $CDCl_3$): $\delta = 4.89$ (t, $J = 13.2$ Hz, 2H), 5.22 (s, 2H), 7.33–7.45 (m, 3H), 7.47–7.57 (m, 2H), 7.93 (dd, $J = 7.3$, 1.4 Hz, 1H),

8.44 (dd, $J=7.3$, 1.4 Hz, 2H); ^{13}C NMR (67.5 MHz, $CDCl_3$): $\delta=60.7$, 80.0, 110.6, 114.4, 123.7, 124.7, 128.5, 129.2, 129.4, 129.9, 133.0, 133.2, 133.9, 136.0, 162.0, 162.1, 162.8; MS: $m/z=679$ [M^+], 660, 649, 573, 554, 530, 280, 174, 91.

Preparation of (2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-Pentadecafluoro)-octyl *N*-Hydroxyphthalimide-4-carboxylate (***F*$_{15}$-NHPI)**

To a solution of **8** (554 mg, 0.82 mmol) in EtOAc (12 mL) was added palladium on activated carbon (10%, 30 mg) under argon. The flask was charged with hydrogen gas, and the solution was stirred under an atmosphere of hydrogen at 45 °C for 4 h. Then the mixture was cooled to room temperature and filtered. The filtrate was evaporated under reduced pressure, and the resulting product was purified by silica gel column chromatography (*n*-hexane/EtOAc = 2/1 to 1/1) and ***F*$_{15}$-NHPI** was obtained in the pure form; yield: 0.393 g (82%). ^{1}H NMR (270 MHz, CD_3OD): $\delta=5.08$ (t, $J=$ 13.5 Hz, 2H), 7.99 (dd, $J=7.6$, 0.5 Hz, 1H), 8.34–8.40 (m, 1H), 8.46 (dd, $J=7.6$, 1.6 Hz, 1H); ^{13}C NMR (67.5 MHz, CD_3OD): $\delta=61.5$, 116.4, 124.6, 124.7, 130.6, 131.2, 131.7, 132.4, 134.9, 135.2, 137.0, 164.4, 164.6; IR (KBr): $\nu=3547$, 2361, 1788, 1721, 1204, 1145, 710 cm^{-1}; anal. calcd. for $C_{17}H_6F_{15}NO_5$: C 34.65, H 1.03, N 2.38; found: C 34.38, H 1.12, N 2.55.

Preparation of 4-(1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-Heptadecafluoro)octyl-*N*-hydroxyphthalimide (***F*$_{17}$-NHPI)**

To a solution of 4-nitrophthalic acid (**9**) (25.0 g) in EtOH (200 mL) was added concentrated H_2SO_4 (10 mL) dropwise and the reaction mixture was stirred at 100 °C for 24 h. After cooling the reaction mixture to room temperature, the organic substances were extracted three times with Et_2O, followed by washing with saturated $NaHCO_3$ solution, and dried over Na_2SO_4. The solvent was evaporated and 4-nitrophthalic acid diethyl ester **10** was obtained as a dark-brown oil; yield: 31.13 g (98%).

To a solution of **10** (31.13 g) in EtOH (400 mL) was added Pd/C (1.02 g) under argon. Then the flask was charged with hydrogen gas and the reaction mixture was stirred for 23 h at room temperature under a hydrogen atmosphere. The reaction mixture was then filtered by using celite, and the filtrate was evaporated under vacuum. The compound 4-aminophthalic acid diethyl ester **11** was obtained as a yellow solid; yield: 25.16 g (91%).

Dilute HCl (200 mL) was added slowly to the flask containing **11** (24.99 g). The reaction mixture was stirred at room temperature for 1 h, and cooled down to −10 °C. Then a solution of $NaNO_2$ (11.18 g) in H_2O (70 mL) was added slowly to the reaction mixture at 5 °C and stirred for 30 min at −10 °C. The resulting mixture was added slowly to another flask containing a solution of KI (35.96 g) in H_2O (300 mL). After finishing the addition, the mixture was stirred for 30 min. Then the organic layer was extracted for 3 times by Et_2O, followed by washing with saturated $Na_2S_2O_3$ solution, and dried over Na_2SO_4. After filtration and evaporation of the solvent, the resulting crude product was purified by silica gel column chromatography with $CHCl_3$ as an eluent and 4-iodophthalic acid diethyl ester **12** was obtained as a brown oil; yield: 29.3 g (80%).

A mixture of **12** (5.01 g), Cu (2.81 g), 2,2-bipyridine (0.48 g) and DMSO (20 mL) was stirred at 110 °C for 32 h under argon. After being cooled down the reaction, it was filtered using celite and the organic substances were extracted with Et_2O, followed by washing with brine and dried over Na_2SO_4. The crude product was purified by silica gel column chromatography using $CHCl_3$ as the eluent to afford **13** as a yellow solid; yield: 7.62 g (83%).

A mixture of **13** (0.50 g), 30% KOH solution (15 mL), and EtOH (10 mL) was stirred at 90 °C for 24 h. Then the reaction mixture was concentrated until the volume was reduced to *ca.* 10 mL and acidified by concentrated HCl. The resulting mixture was then filtered, washed with $CHCl_3$, and evaporated the solvent to afford **14** as a white solid; yield: 0.455 g (99.5%).

A mixture of **14** (2.51 g) and Ac_2O (4 mL) was stirred for 15 min at 150 °C. After cooling to room temperature, the reaction mixture was concentrated. Pyridine (8 mL) and $NH_2OH{\cdot}HCl$ (0.341 g) were added to the resulting solid and stirred for 14 h at 95 °C. After cooling the reaction mixture, it was concentrated and was acidified by concentrated HCl. The resulting mixture was then filtered and washed with $CHCl_3$. A dark-brown solid was obtained, which on recrystallization from EtOH afforded pure ***F*$_{17}$-NHPI** as a pale yellow solid; yield: 1.22 g (49%). ^{1}H NMR (500 MHz, acetone-d_6): $\delta=8.15$ (s, 1H), 8.17 (d, $J=7.8$ Hz, 1H,), 8.27 (d, $J=7.8$ Hz,1H); ^{13}C NMR (125 MHz, acetone-d_6): δ = 121.2, 123.8, 130.5, 133.3, 162.6, 162.7; ^{19}F NMR (471 MHz, acetone-d_6): $\delta=-126.6$, −123.2, −122.3, −122.2, −121.8, −121.5, −110.8, −81.6; IR (KBr): $\nu=3275$, 1786, 1734 cm^{-1}; anal. calcd. for $C_{16}H_4F_{17}NO_3$: C 33.07, H 0.69, N 2.41; found: C 33.05, H 0.77, N 2.64.

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