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Aerobic Oxidation of Cyclopentane by Using Fluorinated *N*-Hydroxyphthalimide Derivatives

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Abstract: *N*-Hydroxyphthalimide derivatives, F_{15}- and F_{17}-NHPI, bearing fluorinated carboxylate and alkyl chains, respectively, were prepared and their catalytic performances were compared with those of *N*-hydroxyphthalimide (NHPI). Thus, the oxidation of cyclopentane under 10 atm of air in the presence of catalytic amount of fluorinated NHPI or NHPI, $Co(OAc)_2$, and $Mn(OAc)_2$ in TFT as solvent at 100°C afforded cyclopentanol, cyclopentanone, succinic acid and glutaric acid. It was assumed that *F*-NHPI derivatives bearing electron withdrawing fluorocarbon groups showed higher catalytic activity than the NHPI by enhancement of the electrophilicity of *N*-oxy radicals generated from the *F*-NHPI derivatives. In the oxidation of cyclopentane, *F*-NHPI showed better catalytic activity than NHPI. Cyclopentanol and glutaric acid were obtained as the major products in case of NHPI, whereas, cyclopentanone and glutaric acid were obtained as the major products in case of fluorinated NHPIs. However, only glutaric acid was obtained as the major product when a increased amount of $Co(OAc)_2$ was used in the present ocidation by using NHPI or *F*-NHPIs. The effect of temperature and air was also investigated in the oxidation of cyclopentane. When the oxidation was performed at 90°C, cyclopentanol was obtained as the major product, whereas, no significant changes were observed when the reaction was performed at 20 atm instead of 10 atm. The great advantage of the fluorinated NHPI derivatives is that it could be recovered after the oxidation.

Keywords: Aerobic Oxidation, Cyclopentane, *F*-NHPI Catalyst, Recovery

1. Introduction

Direct oxidation of hydrocarbons with air (O_2) is a commercially important reaction for the production of oxygen containing compounds such as alcohols, aldehydes, ketones and carboxylic acids which are used in the synthesis of plastics and synthetic fiber materials, polyesters, polycarbonates, and so on. Traditional liquid-phase aerobic oxidation with dioxygen, which is referred to as autoxidation, often suffers from relatively harsh conditions and limited conversion and selectivity [1-3]. Although there have been major advances in the oxidation of saturated hydrocarbons with molecular oxygen, the development of effective and selective methods for the catalytic functionalization of hydrocarbons still remains a major challenge in oxidation chemistry.

Cyclopentane, a flammable hydrocarbon, is a very important raw material for the production of valuable industrial chemicals, such as cyclopentanol, cyclopentanone, and glutaric acid. Till now, a few reports are known for the oxidation of cyclopentane and its derivatives. A very few of those described the catalytic oxidation of cyclopentane. Garetto and Anatoli described the efficient selective oxidation of cyclopentane to glutaric acid over Pt/Al_2O_3 catalysts [4] or by using molecular oxygen [5] in acid solvents. The importance of the cyclopentanol and cyclopentanone cannot be neglected and its production from cyclopentane has also a great industrial value. Mishra and his co-workers described the carbamated silica gel supported bis(maltolato)oxovanadium (IV or V) catalyzed oxidation of cyclopentane to cyclopentanone and cyclopentanol [6]. But due to vigorous reaction conditions it is not economically friendly for industries. Some recent processes are also known which are performed either under harsh conditions or economically unfriendly for the industries or the yields are not satisfactory [7-9].

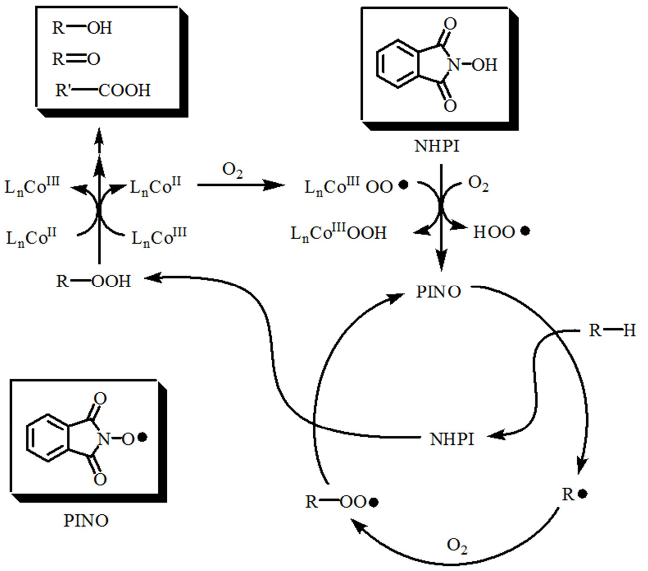

Figure 1. Mechanism for the NHPI catalyzed oxidation of hydrocarbons.

Several NHPI catalyzed oxidation reactions have already been reported [10-15]. It is well known that at first the phthalimide *N*-oxyl radical (PINO) is formed from NHPI, which initiates the catalytic process for oxidation (Figure 1). Due to the low solubility of NHPI in hydrocarbons, some lipophilic NHPI derivatives involving a long alkyl chain were prepared and their catalytic activity was also reported [16]. However, the alkyl chain was found to be oxidized after the oxidation. Very recently, some fluorinated NHPI derivatives were prepared to overcome that problem and their catalytic activity was investigated in the oxidation of cyclohexane [17]. It was found that the fluorinated NHPI derivatives showed better yields for the oxidation reaction and it could be recycled after the oxidation. In the present paper, we are reporting the oxidation of cyclopentane by using fluorinated *N*-hydroxyphthalimide derivatives (*F*-NHPI), F_{15}-NHPI and F_{17}-NHPI, (Figure 2) and the catalytic performances were compared with that of the parent NHPI catalyst.

2. Experimental

2.1. General Methods

Commercially available reagents were used without further purification, unless otherwise noted. GC analysis was performed with a flame ionization detector using a 0.2 mm × 30 mm capillary column (OV-17). The ^{1}H and ^{13}C NMR spectra were recorded on JEOL JNM-LA 300FT (300 MHz for ^{1}H and 67.5 MHz for ^{13}C) NMR spectrometer. The chemical shifts of ^{1}H and ^{13}C NMR are reported on the δ-scale relative to $Si(CH_3)_4$ (δ = 0.00 ppm) as internal standard in $CDCl_3/CD_3OD$ solvent. Infrared (IR) spectra were measured using KBr pellets on a JASCO FT/IR infrared spectrometer and MS spectra were obtained at ionization energy of 70 eV using a JEOL SX-102A mass spectrometer. GC analysis was performed with a flame ionization detector using a 0.2 mm × 30 mm capillary column (OV-17) and the yields of products were estimated from the peak areas on the basis of the internal standard technique by the use of GC.

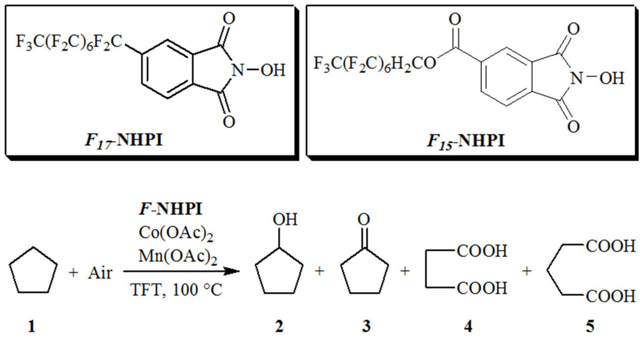

Figure 2. Structure of fluorinated N-hydroxyphthalimides (F-NHPIs) and oxidation of cyclopentane by F-NHPIs.

2.2. Preparation of Fluorinated NHPIs (F-NHPIs)

2.2.1. 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 *O*-benzylhydroxylamine hydrochloride (1.60 g, 10 mmol) in pyridine (32 mL) was added trimellitic anhydride (1.921 g, 10 mmol) slowly at room temperature. When all the trimellitic anhydride was dissolved in the solution, the reaction mixture was refluxed for 14 h. Then it was cooled to room temperature, and acidified with 4M HCl solution. The organic substances were extracted with EtOAc (60 mL × 3), followed by washing with 1M HCl solution, and dried over Na_2SO_4. After evaporating the solvent at reduced pressure, the crude *N*-benzyloxythalimide-4-carboxylic acid (7) (2.7 g, 9.09 mmol) was obtained. Then the compound 7 was dissolved in toluene (50 mL), and thionyl chloride (3.98 ml, 54.54 mmol) and a catalytic amount of DMF (0.1 mL) was 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 get 8. Then, to a suspension of NaH (0.5 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 8 (2.6 g, 8.25 mmol) in THF (30 mL) was added to the reaction mixture. After stirring 1.5 h at 40°C and refluxing for 3 h, the mixture was cooled to room temperature, acidified with 1M 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 9 as pure form (1.91 g, 34% yield in 3 steps). ^{1}H NMR ($CDCl_3$) δ 4.89 (2H, t, J = 13.2 Hz), 5.22 (2H, s), 7.33-7.45 (3H, m), 7.47-7.57

(2H, m), 7.93 (1H, dd, J = 7.3, 1.4 Hz), 8.44 (2H, dd, J = 7.3, 1.4 Hz) ppm; ^{13}C NMR ($CDCl_3$) δ 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 ppm; MS m/z 679 (M^+), 660, 649, 573, 554, 530, 280, 174, 91.

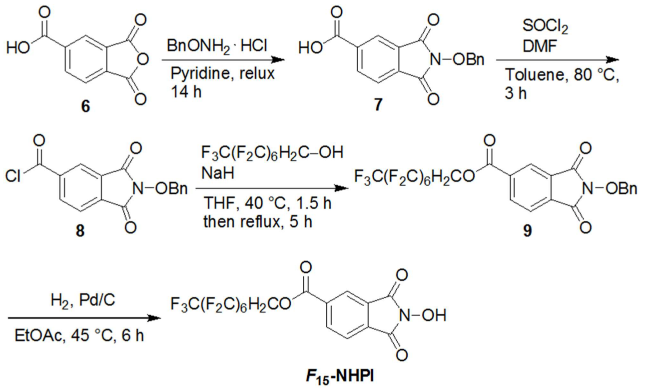

***Figure 3.** Preparation of F_{15}-NHPI.*

To a solution of 9 (554 mg, 0.82 mmol) in EtOAc (12 mL) was added palladium on activated carbon (10%, 30 mg) under Ar. The flask was charged with hydrogen gas, and the solution was stirred under an atmosphere of hydrogen at 45°C for 24 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 82% yield as pure form (0.393 g). ^{1}H NMR (CD_3OD) δ 5.08 (2H, t, J = 13.5 Hz), 7.99 (1H, dd, J = 7.6, 0.5 Hz), 8.34-8.40 (1H, m), 8.46 (1H, dd, J = 7.6, 1.6 Hz); ^{13}C NMR (CD_3OD) δ 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 ppm. IR (KBr) 3547, 2361, 1788, 1721, 1204, 1145, 710 cm^{-1}.

2.2.2. 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 (10) (25.0 g) in EtOH (200 mL) was added conc. H_2SO_4 (10 mL) dropwise and the reaction was stirred at 100°C for 24 h. After cooling down 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 11 was obtained as a dark-brown oil (31.13 g, 98%).

To a solution of 11 (31.13 g) in EtOH (400 mL) was added Pd/C (1.02 g) under Ar. Then the flask was chargedwith hydrogen gas and the reaction mixture was stirred for 23 h at room temperature under hydrogen atmosphere. Then the reaction mixture was filtered by using celite, and the filtrate was evaporated under vacuum. The compound 4-aminophthalic acid diethyl ester 12 was obtained as a yellow solid (25.16 g, 90%).

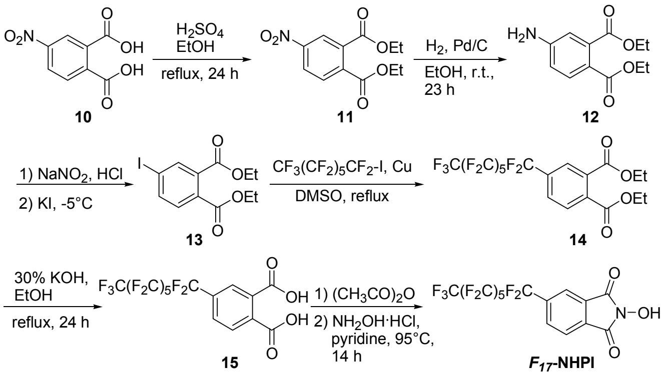

***Figure 4.** Preparation of F_{17}-NHPI.*

Dilute HCl (200 mL) was added slowly to the flask containing 12 (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) and 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 $Na_2S_2O_3$, 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 13 was obtained as brown oil (29.3 g, 80%).

A mixture of 13 (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 Ar. After the reaction, the reaction mixture was filtered by 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 14 as a yellow solid (7.62 g, 83%).

A mixture of 14 (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 came to ca. 10 mL and was acidified by adding conc. HCl. The resulting mixture was then filtered, washed with $CHCl_3$, and evaporated the solvent afforded 15 as a white solid (0.455 g, 99.5%).

A mixture of 15 (2.51 g) and Ac_2O (4 mL) was stirred for 15 min at 150°C. After cooling the reaction mixture at room temperature, the reaction mixture was concentrated. Pyridine (8 mL) and $NH_2OH{\cdot}HCl$ (0.341 g) was added to the resulting solid and stirred for 14 h at 95°C. After cooling the reaction mixture, the mixture was concentrated was acidified by adding conc. 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 (1.22 g, 49%) as a pale yellow solid.

^{1}H NMR (CD_3OD) δ 5.08 (2H, t, J = 13.5 Hz), 7.99 (1H, dd, J = 7.6, 0.5 Hz), 8.34-8.40 (1H, m), 8.46 (1H, dd, J = 7.6, 1.6 Hz); ^{13}C NMR (CD_3OD) δ 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 ppm. IR (KBr) 3547, 2361, 1788, 1721, 1204, 1145, 710

cm^{-1}.

^{1}H NMR (acetone-d_6) δ 8.15 (1H, s), 8.17 (1H, d, J = 7.8 Hz), 8.27 (1H, d, J = 7.8 Hz); ^{13}C NMR (acetone-d_6) δ 121.2, 123.8, 130.5, 133.3, 162.6, 162.7; ^{19}F NMR (acetone-d_6) δ -126.6, -123.2, -122.3, -122.2, -121.8, -121.5, -110.8, -81.6. IR (KBr) 3275, 1786, 1734 cm^{-1}.

2.3. General Procedure for the Oxidation of Cyclopentane (1) Under Air

To a solution of cyclopentane (3.45 mL, ca. 37 mmol) in trifluorotoluene (4 mL) were added NHPI derivatives (0.0125 mmol), $Co(OAc)_2$ and $Mn(OAc)_2$ in a 50 mL teflon-coated autoclave and 10 atm of air was charged in it. After stirring for 6 h at 100°C, it was cooled to room temperature and then diluted with ethanol. GC analysis was performed from that ethanolic solution to determine the amount of cyclopentanol, cyclopentanone and the unreacted cyclopentane. After evaporating under reduced pressure to remove the unreacted cyclopentane, ethanol (10 mL) and a small amount of a conc. sulfuric acid were added to the resulting mixture and stirred at 100°C for overnight. The resulting reaction mixture was cooled to room temperature and GC analysis was performed to determine the yield of glutaric acid and succinic acid.

3. Results and Discussion

The F_{15}-NHPI and F_{17}-NHPI derivatives were prepared according to the procedure described in figures 3 and 4 [14]. The reaction of commercially available trimellitic anhydride (6) with *O*-benzylhydroxylamine hydrochloride afforded *N*-benzyloxyphthalimide-4-carboxylic acid (7). Treatment of 7 with $SOCl_2$ followed by introduction of the fluorinated substituent led to 9, which on subsequent hydrogenation over Pd/C, resulted in F_{15}-NHPI in a total yield of 28% (Figure 3). On the other hand, F_{17}-NHPI was prepared from 4-nitrophthalic acid (10) through a 6-step reaction involving Sandmeyer iodination and a Cu-catalyzed coupling reaction with fluorinated alkyl iodide as the key reactions (Figure 4). The catalytic performance of both NHPI and fluorinated *N*-hydroxyphthalimide derivatives (*F*-NHPI) was examined for the aerobic oxidation of 1 and the results were compared with each other to find out the difference in their catalytic activity.

At first the oxidation of 1 (3.45 mL, 37 mmol) was carried out under air (10 atm) in the presence of NHPI or *F*-NHPI (12.5 μmol), $Co(OAc)_2{\cdot}4H_2O$ (10-20 μmol) and $Mn(OAc)_2{\cdot}4H_2O$ (10 μmol) in trifluorotoluene (TFT) at 100°C for 6 h, affording cyclopentanol (2), cyclopentanone (3), succinic acid (4) and glutaric acid (5). The results are summarized in Table 1. The yields and turn-over number (TON) of the products were measured based on NHPI derivatives used. In the oxidation of 1 by NHPI for 6 h, the yields were 2 (2564%), 3 (1288%), 4 (753%) and 5 (2473%) and the total TON was 70.8. Under the same conditions, F_{15}-NHPI catalyst gave 2 (2812%), 3 (3286%), 4 (884%) and 5 (3044%) with a TON of 100.3 and for F_{17}-NHPI catalyst the yields were 2 (2808%), 3 (3452%), 4 (950%) and 5 (3423%) with a TON of 106.3 (entry 3). These results clearly shows that the *F*-NHPI catalysts were more active than the parent NHPI catalyst in the oxidation of cyclopentane. The higher activity of F_{15}- and F_{17}-NHPI may be due to the fluorinated carboxylate group and fluoroalkyl chain, which possess strong electron-withdrawing character on benzene ring activates the catalytic activity of phthalimide *N*-oxyl (PINO) radical generated from the parent NHPIs (Figure 1). The improved solubility of the *F*-NHPI derivatives in cyclopentane compared with NHPI may be another reason for the higher catalytic activity of *F*-NHPIs.

Among the catalysts examined, it was found that the F_{17}-NHPI catalyst having a long fluoroalkyl chain was the most active catalyst in this oxidation. It is reported that the presence of an electron-withdrawing substituent on the benzene ring of *N*-hydroxyphthalimides enhances the catalytic activity of phthalimide *N*-oxyl radical [18] generated from the parent NHPIs and are therefore known to accelerate the oxidation of hydrocarbons. Thus, it was found that the catalytic activity of NHPI was increased by introducing an electron withdrawing substituent like a fluorinated group. This enhancing effect seems to be higher in case of F_{17}-NHPI than that of F_{15}-NHPI, as the fluorinated chain in F_{17}-NHPI is directly attached to the benzene ring of *N*-hydroxyphthalimide, whereas, the fluorinated chain in F_{15}-NHPI is not directly attached to the benzene ring and is situated a little distance from it. As a result, the F_{17}-NHPI showed better catalytic activity than F_{15}-NHPI. It should be also noted that no oxidation reaction took place in the absence of NHPI or *F*-NHPI derivatives. In the present oxidation, remarkable difference was observed in the production of cyclopentanone and glutaric acid which suggests that the fluorinated catalysts not only make the overall process faster, but also play a strong role in the oxidation of primary oxidized cyclopentanol obtained from cyclopentane and so on. As a result, the yield of cyclopentanone, succinic acid and glutaric acid was also increased in the overall oxidation process. By increasing the amount of $Co(OAc)_2$ under the same condition, that difference become highly remarkable (entries 1-3 vs. entries 4-6 of Table 1). As expected, the yield of the primary oxidized product cyclopentanol is decreased, but the total yield of the products and the TONs of the catalysts were increased. Therefore, it is assumed that the increased amount of Co not only accelerate the oxidation of cyclopentane, but also accelerates the oxidation of cyclopentanol to the further oxidized products cyclopentanone, succinic acid and glutaric acid. Based on these results, a mechanism for the overall oxidation process is proposed in Figure 1 from which the role of Co is clearly understandable. The effect of temperature and air was also investigated in the oxidation of cyclopentane as shown in Table 2.

Table 1. *Aerobic oxidation of cyclopentane (**1**) in trifluorotoluene (TFT) using NHPI derivatives.[a].*

Entry	Catalyst	$Co(OAc)_2$ (mmol)	Yield/%[b]				TON[c]
			2	3	4	5	
1	NHPI	0.01	2564	1288	753	2473	70.8
2	F_{15}-NHPI	0.01	2812	3286	884	3044	100.3
3	F_{17}-NHPI	0.01	2808	3452	950	3423	106.3
4	NHPI	0.02	2414	1816	932	3011	81.7
5	F_{15}-NHPI	0.02	2298	4108	1126	4878	124.1
6	F_{17}-NHPI	0.02	2335	4598	1098	5071	131.0

[a] Compound 1 (37 mmol) was allowed to react in TFT under air (10 atm) at 100°C in the presence of NHPI or *F*-NHPI (12.5 µmol), $Co(OAc)_2 \cdot 4H_2O$ (10/20 µmol) and $Mn(OAc)_2 \cdot 4H_2O$ (10 µmol).
[b] GC yield based on the catalyst used.
[c] TON = 2+3+4+5 (mmol) / Catalyst (mmol).

Table 2. *Effect of temperature and pressure in the aerobic oxidation of cyclopentane (**1**).[a].*

Entry	Catalyst	Temperature (°C)	Air (atm.)	Yield/%[b]				TON[c]
				2	3	4	5	
1	NHPI	100	10	2414	1816	932	3011	81.7
2	F_{15}-NHPI	100	10	2298	4108	1126	4878	124.1
3	F_{17}-NHPI	100	10	2335	4598	1098	5071	131.0
4	NHPI	90	10	3576	1200	145	297	52.2
5	F_{15}-NHPI	90	10	3876	3326	357	755	83.1
6	F_{17}-NHPI	90	10	4184	3784	411	1166	95.5
7	NHPI	100	20	2018	2529	587	2952	80.9
8	F_{15}-NHPI	100	20	2778	4324	933	3862	119.0
9	F_{17}-NHPI	100	20	2939	4521	1434	4588	134.8

[a] Compound 1 (37 mmol) was allowed to react in TFT under air (10 atm) at 100/90°C in the presence of NHPI or *F*-NHPI (12.5 µmol), $Co(OAc)_2 \cdot 4H_2O$ (20 µmol) and $Mn(OAc)_2 \cdot 4H_2O$ (10 µmol).
[b] GC yield based on the catalyst used.
[c] TON = 2+3+4+5 (mmol) / Catalyst (mmol).

When the reaction was performed at 90°C, cyclopentanol was obtained as the major product. In this case also, *F*-NHPIs showed better catalytic activity than the parent NHPI, which can be easily understood from the individual yield of the oxidized products and also from the total TON (entries 4-6, Table 2). The amount of cyclopentanone, succinic acid and glutaric acid is remarkably lower than that obtained at 100°C, which clearly proves that temperature plays a very important role in the oxidation of cyclopentanol to other oxidized products. The total TON at 90°C was also lower than that at 100°C indicating the slower reaction at lower temperature (entries 4-6 vs. entries 1-3, Table 2). After observing the effect of temperature, the effect of air was also investigated (entries 7-9) at 100°C. No significant changes were observed when the reaction was performed at 20 atm instead of 10 atm.

4. Conclusions

In conclusion, we have developed an efficient method for the catalytic aerobic oxidation of cyclopentane, in which fluorinated NHPI catalysts showed better results compared with NHPI. The advantages of the *F*-NHPI is that it can be recovered after the oxidation and the reaction can be performed in a mild condition. In addition, by changing the reaction temperature the choice for the production of major product can be changed. We believe that the above procedure will be an efficient method for the chemical and other industries to get the selective oxidized products of cyclopentane. It is mild, cheap, easier and very effective. Further progress of the work is now going on and will be reported in due time.

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