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N-Hydroxyphthalimide (NHPI)-Catalyzed Reaction of Adamantane Under Nitric Oxide Atmosphere

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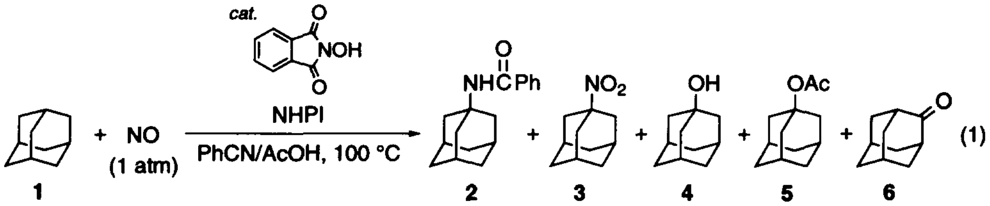
Abstract : The reaction of adamantane under atmospheric nitric oxide in the presence of *N*-hydroxyphthalimide (NHPI) which serves as the radical catalyst in a mixed solvent of benzonitrile and acetic acid afforded 1-*N*-adamantylbenzamide as a principal product along with small amounts of 1-nitroadamantane and 1-hydroxyadamantane. On the other hand, 1-nitroadamantane was obtained in good yield upon treatment of adamantane with NO/O_2. © 1997 Elsevier Science Ltd.

In recent years, there has been much interest in nitration and oxidation using nitrogen oxides such as nitric oxide (NO),[1] nitrogen dioxide (NO_2),[2] and nitrous oxide (N_2O)[3] as nitration and oxidation reagents. More recently, Suzuki *et al.* have reported the nitration of adamantane (**1**) to 1-nitroadamantane (**3**) with NO_2 in the presence of ozone.[4]

In a previous paper, we showed that **1** can be selectively hydroxylated with dioxygen (1 atm) using a catalytic amount of *N*-hydroxyphthalimide (NHPI) and Co(acac)$_n$ (n = 2 or 3) to give 1-hydroxyadamantane (**4**) and 1,3-dihydroxyadamantane under mild conditions.[5] In a continuation of our study on the oxidation of alkanes using NHPI as the catalyst, we wish herein to report the NHPI-catalyzed reaction of **1** under the influence of NO.



A typical reaction was carried out as follows: To a solution of **1** (1 mmol) in benzonitrile (6 mL) and acetic acid (1.2 mL) in a three necked flask was added NHPI (0.1 mmol) and allowed to react under an atmospheric pressure of NO at 100 °C for 20 h. After removing the solvent *in vacuo*, the products were isolated by column chromatography (silica gel, chloroform eluent).

Table 1 shows the representative results for the reaction of **1** using NHPI as a catalyst under NO atmosphere in various solvents. The reaction of **1** with NO (1 atm) in the presence of NHPI (10 mol%) in a mixed solvent of benzonitrile and acetic acid at 100 °C gave 1-*N*-adamantylbenzamide (**2**)[6] in substantial yield (65%) along with

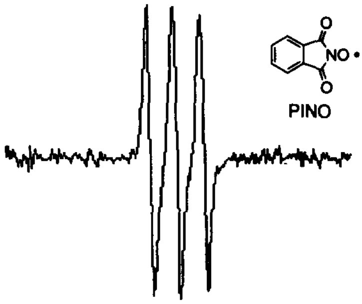
Table 1. Reaction of Adamantane (1) Catalyzed by *N*-Hydroxyphthalimide (NHPI) under NO Atmosphere in Various Solvents[a]

Run	Solvent (mL/mL)	Conv. (%)	Products (Yield / %)				
			2	**3**	**4**	**5**	**6**
1	PhCN/AcOH (6.0/1.2)	92	65	6	7	2	2
2[b]	PhCN/AcOH (6.0/1.2)	<5	<1	<1	<1	<1	–
3[c]	PhCN (7.2)	25	14	2	6	–	<1
4[d]	AcOH (7.2)	88	–	30	8	29	2
5[e]	PhCN/AcOH (6.0/1.2)	87	48	6	5	1	2
6[f]	MeCN/AcOH (6.0/1.2)	49	**7** (33)	4	5	7	1
7[g]	PhCN/AcOH (6.0/1.2)	26	6	4	3	3	1

[a] **1** (1 mmol) was allowed to react in the presence of NHPI (0.1 mmol) under NO atmosphere at 100 °C for 20 h. [b] In the absence of NHPI. [c] 2 h. [d] 3 h. [e] NHPI (0.05 mmol). [f] 75 °C. [g] $Co(acac)_2$ (0.01 mmol) was added.

small amounts of nitroadamantane (**3**), **4**, 1-acetoxyadamanatne (**5**), and 2-adamantanone (**6**) (Table 1, run 1). Although there are a few reports on the transformation of **1** to **2** by means of the anodic oxidation[8a] or nitronium tetrafluoroborate[8b] in benzonitrile, the present reaction is the first example for the preparation of **2** *via* the catalytic process. In the absence of NHPI, trace amounts of products were formed (run 2). The reaction of **1** in benzonitrile alone at 100 °C for 2 h produced **2** (14%) and **4** (6%) in 25% conversion (run 3), but a prolonged reaction resulted in a complex mixture of products. In acetic acid, **3** (30%) and **5** (29%) were obtained as major products together with small amounts of **4** as well as 1,3-diacetoxyadamantane (5%) and 1-acetoxy-3-nitroadamantane (6%) (run 4). When the amount of NHPI was halved from 10 mol% to 5 mol%, **2** was obtained in a slightly lower yield (48%) (run 5). In a mixed solvent of acetonitrile and acetic acid, 1-*N*-adamantylacetoamide (**7**) was formed in 33% yield (run 6). In contrast to the NHPI-catalyzed oxidation of **1** with dioxygen where the reaction is significantly enhanced by the addition of transition metal salts such as $Co(acac)_2$ and $VO(acac)_2$, the present reaction was markedly inhibited by the addition of $Co(acac)_2$ (run 7). It is well known that NO easily reacts with various metal ion complexes to form NO-complexes.[9] Consequently, it seems that a certain Co-NO complex generated *in situ* from $Co(acac)_2$ and NO inhibits the desired reaction.

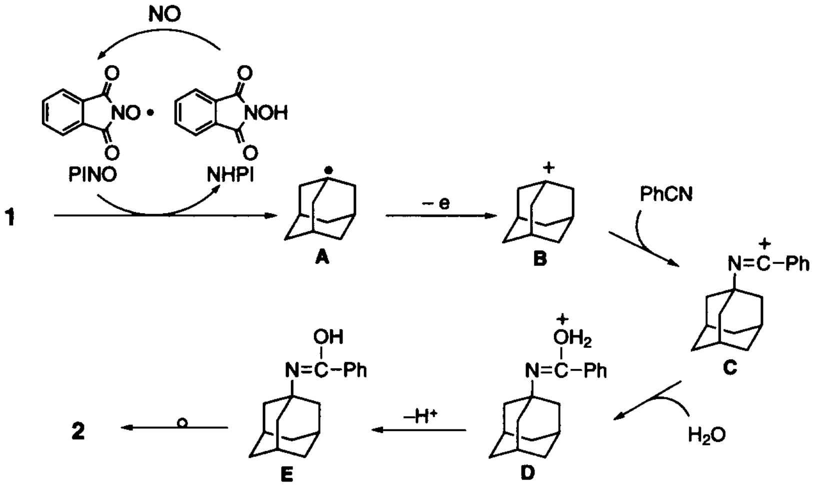
Due to the complexity of the reaction system, it seems rather difficult to make an accurate assessment of the present transformation of **1** to **2** by the NHPI-NO system. However, since NO is a free radical involving an unpaired electron,[10] it is probable that the NHPI reacts with NO in a similar way as that with O_2 to generate phthalimide *N*-oxyl (PINO) which is a key species in the NHPI-catalyzed reactions.[11] Indeed, an ESR signal based on PINO[12] could be observed as a triplet signal by exposing NHPI to NO in benzonitrile at 100 °C (Figure 1).[13] In addition, Janzen *et al.* report that NO can abstract the phenolic hydrogen of phenol to form phenoxyl radical.[1g,h]



(g = 2.0073, A_N = 4.23 G)

Figure 1. ESR Spectrum of PINO Obtained by Exposing NHPI to NO

Scheme 1. A Possible Reaction Path for the NHPI-Catalyzed Reaction of Adamantane (1) under NO Atmosphere in Benzonitrile



Consequently, the following reaction path which involves an adamantyl cation through the formation of adamantyl radical as the intermediate is proposed for the production of **2** in benzonitrile (Scheme 1).

The reaction is believed to proceed *via* the generation of PINO from NHPI and NO in the benzonitrile. The resulting adamantyl radical (**A**) appears to be converted into tertiary adamantyl cation (**B**) by single-electron transfer to an appropriate electron acceptor such as NO. Indeed, in the reaction of nitric oxide with amines, Ohsawa *et al.* have reported that the reaction is initiated by one-electron transfer from amines to NO.[1m] Furthermore, tertiary radicals such as adamantyl radical **A** are reported to be easily converted into tertiary carbonium ions.[14,15] Subsequently, the **B** is captured by benzonitrile and then water to form amide **2**. The process is analogous to the Ritter reaction. When the reaction was carried out in acetic acid, nitroadamantane **3** and acetoxyadamantane **5** were formed as principal products. This may be due to the competition between the coupling reaction of **A** with NO and the oxidation of **A** to **B**, to produce **3** and **5**, respectively.

To examine the influence of dioxygen on the NHPI-catalyzed reaction of **1** with NO, the reaction of **1** in the presence of NO and O_2 was performed. Hirobe *et al.* have reported that the conversion of aromatic amines to the corresponding triazenes by NO in the presence of O_2.[1k] The reaction of **1** with a 1 : 1 mixture of NO and O_2 catalyzed by NHPI (10 mol%) in 1,2-dichloroethane and acetonitrile (5/1 v/v %) afforded nitroadamantane **3** in good yield. Furthermore, the reaction was found to take place even in the absence of NHPI, forming **3** in substantial yield (eq. 2).

In conclusion, the catalytic transformation of **1** to amide **2** was achieved. In the reaction of **1** with NO/O_2

$$\mathbf{1} + \underset{(1\ \text{atm})}{NO - O_2} \xrightarrow[(CH_2Cl)_2/CH_3CN,\ 60\ ^\circ C,\ 8\ h]{cat.\ NHPI\ (10\ mol\%)} \mathbf{3} + \mathbf{4} + \mathbf{6} \qquad (2)$$

Conv. 90 (70)% 70 (65)% 3 (2)% 4 (2)%

( ) without NHPI

in the presence or absence of NHPI, **3** was obtained in good yield. Further application and mechanistic studies of the present reaction are now underway.

Acknowledgment

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6 Spectral data of **2**; ^{1}H-NMR ($CDCl_3$ /Me_4Si) δ 7.65-7.61 (m, 2 H), 7.38-7.28 (m, 3H), 5.75 (br, 1 H), 2.05 (br, 9 H), 1.69 (br, 6 H); ^{13}C-NMR ($CDCl_3$ / Me_4Si) δ 166.5, 136.0, 130.9, 128.3, 126.6, 52.2, 41.6, 36.3, 29.4; IR (KBr) 3322, 2914, 1744, 1633, 1537, 1488, 1344, 1251, 807, 717 cm^{-1}; m.p. 148-150 °C (lit.[7] 151-152 °C).

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