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An Efficient Nitration of Light Alkanes and the Alkyl Side-Chain of Aromatic Compounds with Nitrogen Dioxide and Nitric Acid Catalyzed by *N*-Hydroxyphthalimide

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Nitration of light alkanes and the alkyl side-chain of aromatic compounds with NO_2 and HNO_3 was successfully achieved by the use of *N*-hydroxyphthalimide (NHPI) as a catalyst under relatively mild conditions. For example, the nitration of propane with NO_2 catalyzed by NHPI at 100 °C for 14 h gave 2-nitropropane in good yield without formation of 1-nitropropane and cleaved products such as nitroethane and nitromethane. Various aliphatic nitroalkanes, which are difficult to prepare by conventional methods, could be selectively obtained by means of the present methodology by using NHPI as the key catalyst. In addition, the side-chain nitration of alkylbenzenes such as toluene was selectively carried out to lead to α-nitrotoluene without the ring nitration. The present reaction provides an efficient selective method for the nitration of light alkanes and alkylbenzenes, which has been very difficult to carry out so far.

Introduction

Nitration of saturated hydrocarbons is a fundamental and important reaction in synthetic and industrial organic chemistry.[1] Despite their practical importance, however, useful methods for the nitration of aliphatic hydrocarbons have been rarely developed in contrast to the nitration of aromatic hydrocarbons. Currently, nitration of light alkanes by nitrogen dioxide or nitric acid as a nitrating reagent is operated at higher reaction temperature (200−350 °C) to generate thermally alkyl radicals by the C−H bond scission of alkanes.[2] The reaction under such forced conditions, however, would cause undesired C−C bond scissions, since the bond dissociation energy of the C−C bonds of alkanes is rather lower than that of the C−H bonds. Therefore, the large-scale nitration of alkanes has been limited to several lower alkanes such as methane, ethane, and propane. For example, it has been reported that the nitration of propane with NO_2 at 300 °C produces 1- and 2-nitropropanes along with cleaved nitro compounds such as nitroethane and nitromethane in 26% total yield based on NO_2 used.[3] Although attempts to improve the conversion and selectivity to nitroalkanes by adding an additive such as oxygen, ozone, or halogen have been made, these additives promote not only the generation of alkyl radicals but also the production of oxygenated or halogenated compounds.[2] For the nitration of adamantanes, several methods have been developed so far. Olah et al. have shown the nitration with nitronium salts in nitromethane.[4] Photoinduced nitration with N_2O_5 is reported to produce an approximately 1:1 mixture of nitroadamantane and adamantane nitrite.[5] Recently, Suzuki et al. have presented a novel nitration using NO_2 assisted by ozone,[6] although this strategy is limited to the nitration of adamantane and its derivatives. Hence, a new general strategy for the nitration of alkanes with NO_2 has been desired for a long time, in particular, in the chemical industry.

In the course of our studies on the development of aerobic oxidation of alkanes catalyzed by *N*-hydroxyphthalimide (NHPI),[7] we have recently disclosed in communications[8] a practical and versatile catalytic method for the nitration of cyclohexane and adamantane with NO_2 or HNO_3 in the presence of NHPI . In this paper, we wish to report our recent results for the selective nitration of light alkanes and the alkyl side-chain of aromatic compounds by NO_2 or HNO_3 with NHPI as a key catalyst.

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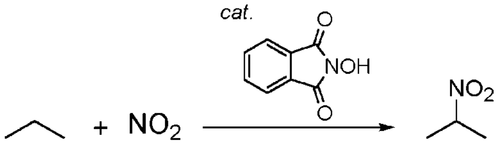
TABLE 1. Nitration of 1 Catalyzed by NHPI[a]

run	NHPI/mmol	temp/°C	yield/%[b]
1	0.3	100	65
2	0	100	12
3	0.15	100	37
4[c]	0.3	100	36
5	0.3	70	37
6	0.3	50	6
7[d]	0.3	100	58
8[d]	0.6	100	62

[a] **1** (5 atm) was allowed to react with NO_2 (1.6 mmol) in the presence of NHPI and air (1 atm) in $PhCF_3$ (5 mL) with use of a glass autoclave for 14 h. [b] Based on a nitrating reagent used. [c] Reaction was carried out without air. [d] Concentrated HNO_3 (1.5 mmol) was used instead of NO_2.

Results and Discussion

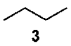
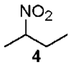
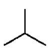
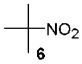
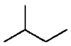
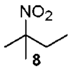
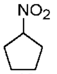
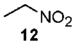
1. Nitration of Light Alkanes. To a glass autoclave containing 0.3 mmol of NHPI and 1.6 mmol of NO_2 in $PhCF_3$ were charged air (1 atm) and propane (**1**) (5 atm). After the reaction mixture was stirred at 100 °C for 14 h, 2-nitropropane (**2**) was obtained in 65% yield based on NO_2 used (eq 1). It is interesting to note that the secondary C−H bond of **1** was selectively nitrated, although the conventional nitration of **1** provided all possible nitrated products.[3] Furthermore, other nitrated products such as nitroethane and nitromethane caused by the C−C bond cleavage of the **1** were not detected at all under these reaction conditions. To the best of our knowledge, this is the first successful selective nitration of propane to **2** without formation of other nitrated compounds. The most important point leading to the high selectivity in this nitration is that the reaction can be operated at a lower temperature (<100 °C).



1 **2** (1)

Table 1 summarizes the representative results for the nitration of **1** catalyzed by NHPI. The reaction of **1** with NO_2 lacking NHPI led to **2** in poor yield (Run 2). The formation of the nitrated products other than **2** could not be detected under these reaction conditions, although the nitration of **1** with NO_2 at higher reaction temperature (300 °C) gave not only **2** and 1-nitropropane but also C−C bond-cleavage products such as nitroethane and nitromethane.[3] When the amount of NHPI was halved, the yield of **2** decreased to 37% (Run 3). Removal of air from the reaction system resulted in a low yield of **2** as discussed later (Run 4). The optimum reaction temperature was found to be 100 °C for **1** (Runs 5 and 6). The nitration was also carried out by the use of commercially available *concentrated* nitric acid instead of NO_2 as a nitrating reagent. It is important that HNO_3 can be employed as a nitrating reagent in place of NO_2, since HNO_3 is readily available and easily handled. The reaction of **1** (5 atm) with HNO_3 (1.5 mmol) in the presence of a catalytic amount of NHPI (0.6 mmol) in a glass autoclave afforded **2** in 62% yield, which is comparable to that of the nitration with NO_2 (Run 8). In this reaction, nitrated products other than **2** were not formed in the same way as the nitration with NO_2.

TABLE 2. Nitration of Several Light Alkanes by NHPI[a]

Run	Substrate	Reagent (mmol)	Conditions (atm)	NHPI (mmol)	Product	Yield[b] (%)
1[c]	 **3**	NO_2 (3.2)	Air (2)	0.6	 **4**	65
2	 **5**	NO_2 (2.4)	Air (2)	0.6	 **6**	61
3	**5**	HNO_3 (1.5)	Air (1)	0.2	**6**	60
4[d]	 **7**	NO_2 (3.2)	Air / N_2 (1/4)	0.6	 **8**	73
5[e]	**7**	HNO_3 (1.5)	Air / N_2 (0.2/0.8)	0.2	**8**	70
6	 **9**	HNO_3 (1.5)	Air (1)	0.2	 **10**	70
7[f]	CH_3CH_3 **11**	NO_2 (2.5)	Air (1)	0.3	 **12**	28

[a] Substrate (2 mL of **3** and **5** or 5 mL of **7** and **9**) was allowed to react with NO_2 or HNO_3 in the presence of NHPI under air or a mixed gas of air/N_2 in $PhCF_3$ (5 mL) with use of a glass autoclave at 70 °C for 14 h. [b] Based on a nitrating reagent used. [c] 100 °C. [d] 50 °C. [e] 60 °C, 5 h. [f] Ethane (5 atm) was allowed to react with NO_2 in $PhCF_3$ (10 mL) at 130 °C for 14 h.

On the basis of these results, several light alkanes were allowed to react with NO_2 or HNO_3 in the presence of the NHPI catalyst under selected reaction conditions. Representative results after screening the reaction conditions are summarized in Table 2. *n*-Butane (**3**) was nitrated with NO_2 to afford 2-nitrobutane (**4**) in 65% yield (Run 1). The formation of 1-nitrobutane was found to be negligible. The nitration of isobutane (**5**) and 2-methylbutane (**7**) by the NHPI/NO_2 system occurred selectively at their tertiary positions, giving the corresponding nitro compounds, 2-methyl-2-nitrobutane (**6**) and 2-methyl-2-nitrobutane (**8**), in 61% and 73% yields, respectively (Runs 2 and 4). The nitration of cyclopentane (**9**) by the NHPI/HNO_3 system gave nitrocyclopentane (**10**) in 70% yield without any side products caused by a ring-opening reaction (Run 6). It is interesting to note that the NHPI/NO_2 system could be applied to the nitration of ethane (**11**). Treatment of **11** with NO_2 catalyzed by NHPI at 130 °C led to nitroethane (**12**) in 28% yield, but nitromethane was not observed (Run 7). Unfortunately, methane was difficult to nitrate under these conditions.

To compare the reactivity between the secondary C−H bond and the tertiary bond, a 1:1 mixture of **3** and **5** (total pressure of 1.5 atm) was reacted with NO_2 (3.2 mmol) under the influence of NHPI (0.6 mmol) and air (1 atm) in $PhCF_3$ in a 50-mL glass autoclave at 50 °C (Figure 1). It was found that the methine group in **5** was nitrated in preference to the methylene group in **3**. After 2 h at this stage of the reaction, **6** was obtained in 21% yield, while the nitration of **3** to **4** was less than 1%. After 14 h, **4** and **6** were obtained in 6% and 52% yields, respectively.

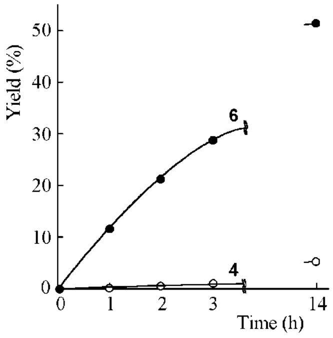
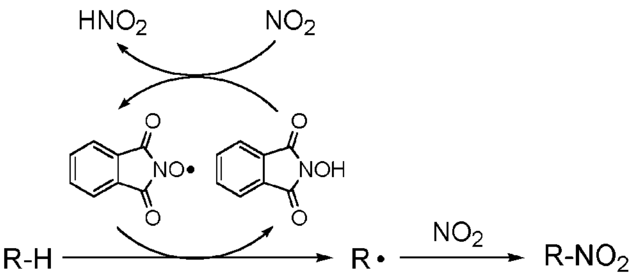
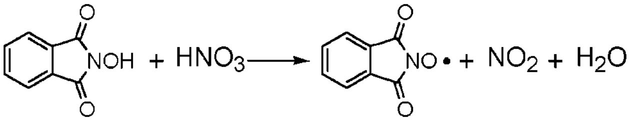


FIGURE 1. Time dependence curve for nitration of **3** and **6** with the NHPI/NO_2 system at 50 °C.

SCHEME 1



SCHEME 2

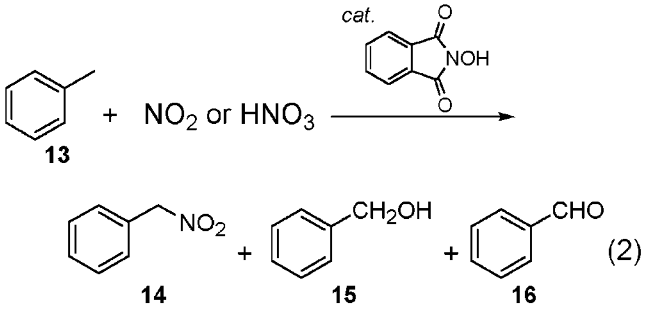


A plausible reaction path is proposed in Scheme 1. The nitration may be initiated by the hydrogen atom abstraction from the hydroxyimide group of NHPI by NO_2 to generate a PINO radical. The ESR measurement of the reaction of NHPI with NO_2 indicated a triplet signal that is assigned to the PINO radical.[9] The PINO readily abstracts the hydrogen atom from an alkane to form an alkyl radical that undergoes nitration with NO_2 to give a nitroalkane. It is reported that HNO_2 is converted into HNO_3, H_2O, and NO.[10] Therefore, the nitration of **1** by an NO_2/air system produced **2** in higher yield than that by NO_2 alone. Under our conditions, the NO formed is expected to be oxidized by air to NO_2, and the generated NO_2 is reused in the present nitration. In the NHPI-catalyzed nitration of alkanes with HNO_3, the reaction is initiated by the reaction of HNO_3 with NHPI to generate PINO and NO_2 (Scheme 2) and the resulting NO_2 reacts with alkyl radicals, generated by the hydrogen abstraction from alkanes by PINO, to produce nitroalkanes.

Thus, the first selective nitration of light alkanes with NO_2 or HNO_3, which has been desired for a long time in the chemical industry, was successfully accomplished by the use of NHPI as the radical- producing catalyst from alkanes.

2. Side-Chain Nitration of Alkylbenzenes. The introduction of a nitro group to an aromatic ring is usually referred to as nitration and is a well-established method in organic chemistry.[11] The nitration of aromatic compounds is easily achieved by using nitric acid in the presence of sulfuric acid. Recent progress in nitration of aromatic compounds has been made by Suzuki et al., who employed an NO_2/O_3 system as the nitrating agent.[12] Kochi et al. studied the thermal and photochemical nitration of aromatic hydrocarbons with NO_2 in dichloromethane.[13] In contrast to these nitrations leading to nitro compounds in which the NO_2 group is incorporated into their aromatic rings, the nitration of the alkyl side-chain of aromatic compounds is difficult to carry out by the conventional methods. Thus, we next examined the selective nitration of the alkyl side-chain of aromatic compounds, which still remains as an unsolved subject in synthetic organic chemisty, with HNO_3 or NO_2 using the NHPI catalyst.

A mixture of toluene (**13**) (5 mL), *concentrated* HNO_3 (1.5 mmol), and NHPI (0.2 mmol) was stirred at 60 °C under argon for 5 h to produce α-nitrotoluene (**14**) (60%) as a major product along with oxygenated products, benzyl alcohol (**15**) (21%) and benzaldehyde (**16**) (19%) (eq 2). Table 3 shows the representative results for the nitration of **13** with HNO_3 and NO_2 by NHPI catalyst under various reaction conditions.



The methyl moiety of **13** was successfully nitrated with *concentrated* HNO_3 by NHPI at 60 °C (Method A) to form **14** in satisfactory yield with oxygenated products, **15** and **16**, because of the high oxidizing potential of HNO_3 (Run 1). It is important to note that almost no nitration of the benzene ring was observed under these conditions. The same reaction in the absence of NHPI afforded these products in very low yields even after 15 h (Run 2). In a previous paper, we showed that *N*-acetoxyphthalimide (NAPI) undergoes hydrolysis with water to supply gradually NHPI during the reaction.[14] Thus, the nitration by the use of NAPI in place of NHPI at 60 °C was examined, but the nitration by the NAPI proceeded slowly to form **14** in moderate yield (Run 3). Thus, the reaction was carried out at higher temperature (90 °C) for 15 h, giving **14** in 62% yield (Run 5). In contrast, the nitration by

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TABLE 3. Nitration of Toluene (13) with HNO_3 or NO_2 by NHPI or NAPI under Several Conditions[a]

run	catalyst	method/temp/time (°C) (h)	product yield (%) **14**	**15**	**16**
1	NHPI	**A**/60/5	60	21	19
2		**A**/60/15	11	3	4
3	NAPI	**A**/60/5	37	15	7
4	NAPI	**A**/90/5	54	17	13
5	NAPI	**A**/90/15	62	16	14
6	NHPI	**A**/90/1	53	19	17
7	NHPI	**B**/60/5	46	14	19
8	NAPI	**B**/60/5	25	9	3
9	NAPI	**B**/90/5	62	10	14
10	NAPI	**B**/90/15	68	14	13
11	NHPI	**B**/90/5	43	11	23
12	NAPI	**C**/90/15	13	trace	trace

[a] Method **A**: **13** (5 mL) was reacted with concentrated HNO_3 (1.5 mmol) with NHPI or NAPI (0.2 mmol) under argon. Method **B**: **13** (5 mL) was reacted with NO_2 (3.2 mmol) with NHPI or NAPI (0.6 mmol) under air. Method **C**: **13** (3 mmol) was reacted with NO_2 (3.2 mmol) with NHPI (0.6 mmol) under air in $PhCF_3$ (5 mL).

NHPI at 90 °C was completed within 1 h to form **14**, **15**, and **16** in 53%, 19%, and 17% yields, respectively (Run 6).

On the other hand, the nitration of **13** with NO_2 under air (Method B) by the use of NHPI or NAPI is summarized in Runs 7 to 11. The nitration was successfully carried out by NO_2 in the presence of NHPI or NAPI. The best yield of **14** was obtained in the nitration of **13** with NO_2 by using NAPI as the catalyst (Run 10). The nitration of **13** with NO_2 in $PhCF_3$ (method C) was considerably retarded to form **14** in a low yield (13%), although almost no oxygenated products were formed (Run 12).

Conventionally, **14** is prepared by several methods, e.g. (i) reaction of silver nitrite with benzyl halide,[15] (ii) substitution of benzyl alcohol by sodium nitrite,[16] (iii) dry ozonation of benzylamine,[17] (iv) oxidation of benzaldoxime by Mo(VI) oxodiperoxo complex,[18] etc., but the present direct nitration of **13** seems to be the best approach to **14** taking into account the ease of the reaction and the yield of the product **14**.

To know the nitrating ability of NHPI and NAPI, the time dependence for the nitration of **13** with HNO_3 by NAPI was compared to that by NHPI (Figure 2). The nitration of **13** proceeded rapidly by NHPI and was completed within about 2 h. However, the yield of **14** by NAPI increased gradually along with the progress of time. This shows that NAPI slowly undergoes hydrolysis to NHPI, which then catalyzes the nitration of **13**. As shown previously, a large amount of NHPI at the chain propagation step resulted in the over-generation of the PINO, which induces the decomposition of PINO to phthalimide and phthalic anhydride, leading to low yield of the products.[14] In the reaction with NAPI, the gradual generation of NHPI from NAPI would prevent the over-generation of PINO during the reaction. Hence, it is thought that NAPI controlled the formation of PINO at the propagation step. On the basis of these results, several aromatic compounds were nitrated with HNO_3 and NO_2 by NAPI and/or NHPI under selected reaction conditions (Table 4).

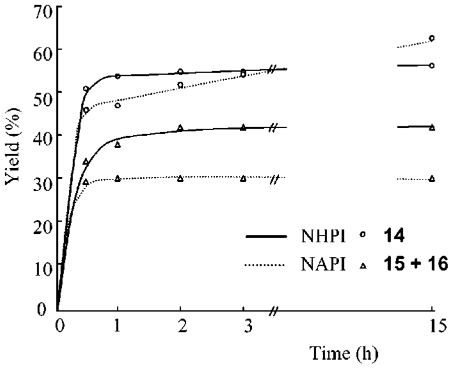

FIGURE 2. Time dependence curve for nitration of **13** with HNO_3 catalyzed by NHPI or NAPI at 90 °C.

The reaction of ethylbenzene (**17**) with NO_2 under air by NHPI afforded α-nitroethylbenzene (**18**) (28%) and an oxidized product, acetophenone (**19**) (49%), as well as a cleaved product, **15** (52%) (Run 1). Previously, we reported that the NHPI-catalyzed aerobic oxidation of methylquinoline was accelerated by adding a small amount of NO_2 as an initiator.[19] It seems likely that the formation of **15** and **19** can be explained by the reaction of the corresponding benzylic radical derived from **17** with dioxygen. The reaction by NAPI led to a slight increase of **18** (Run 2). Since **17** was found to be a reactive substrate, the reaction was carried out in $PhCF_3$ using NHPI and NAPI as catalysts to suppress over-reaction. Thus, **18** was obtained in satisfactory yields, 63% by NHPI and 58% by NAPI, as a major product (Runs 3 and 4). Upon treatment of cumene (**20**) with NO_2 or HNO_3 under the influence of NHPI, α-nitroisopropylbenzene (**21**), cumyl alcohol (**22**), and isopropenylbenzene (**23**) were obtained (Runs 5 and 6). In these reactions, owing to the increase of the electron density of the benzene ring substituted by the electron-donating isopropyl group, a mixture of *o*- and *p*-isopropylnitrobenzenes by the ring nitration was formed in 5−10% yields.

o-Xylene (**24**) was nitrated with HNO_3 by NAPI to give mononitrated product (**25**), and oxygenated products such as aldehyde (**27**) and alcohol (**26**) (Run 7). In a similar manner as **24**, *m*- and *p*-xylenes, **28** and **32**, produced the corresponding nitrated products in satisfactory yields along with oxygenated products (Runs 8 and 9). Mesitylene (**36**) was nitrated with NO_2 in $PhCF_3$ to form a mononitrated product (**37**) as a major product (Run 10). It was found that **36** is nitrated with NO_2 in the absence of NHPI to give nitromesitylene (**38**) as a major product (Run 11). *p*-Chrolotoluene (**39**) was nitrated by NAPI/NO_2 to form *p*-chrolo-α-nitrotoluene (**40**) in 69% yield (Run 12).

In conclusion, we have successfully achieved the nitration of light alkanes and the alkyl side-chain of aromatic compounds with NO_2 or HNO_3 by the use of NHPI as the catalyst. This reaction provides a versatile selective method for the preparation of a variety of nitroalkanes as well as α-nitrated alkyl aromatic compounds.

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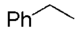
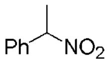
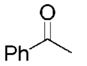
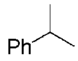
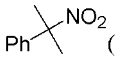
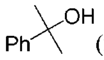
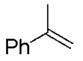
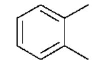
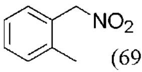
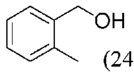
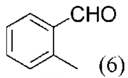
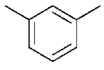
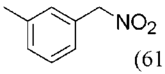
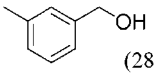
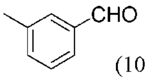
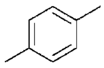
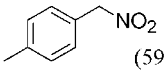
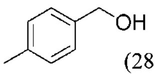
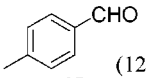
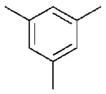
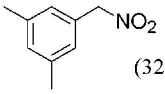
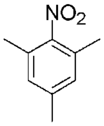
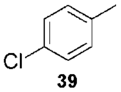
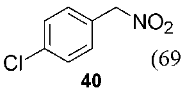
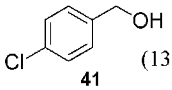
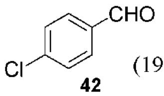
TABLE 4. Nitration of Aromatic Compounds with HNO_3 or NO_2 by NHPI and NAPI under Several Conditions[a]

Run	Sunstrate	Catalyst	Method / Temp. / Time (C) (h)	Product / Yield (%)		
1	 **17**	NHPI	**B** / 90 / 5	 **18** (28)	 **19** (49)	**15** (52)
2	**17**	NAPI	**B** / 90 / 5	**18** (36)	**19** (49)	**15** (50)
3	**17**	NHPI	**C** / 90 / 14	**18** (63)	**19** (26)	**15** (7)
4	**17**	NAPI	**C** / 90 / 14	**18** (58)	**19** (21)	**15** (6)
5[b]	 **20**	NHPI	**B** / 70 / 5	 **21** (55)	 **22** (28)	 **23** (13)
6	**20**	NHPI	**A** / 60 / 15	**21** (41)	**22** (20)	**23** (2)
7	 **24**	NAPI	**A** / 90 / 5	 **25** (69)	 **26** (24)	 **27** (6)
8	 **28**	NAPI	**A** / 90 / 5	 **29** (61)	 **30** (28)	 **31** (10)
9	 **32**	NAPI	**A** / 90 / 5	 **33** (59)	 **34** (28)	 **35** (12)
10	 **36**	NAPI	**C** / 70 / 5	 **37** (32)	 **38** (2)	
11	**36**	-	**C** / 70 / 5	**37** (14)	**38** (22)	
12	 **39**	NAPI	**C** / 90 / 15	 **40** (69)	 **41** (13)	 **42** (19)

[a] See Table 3, footnote *a*. [b] **19**, isopropyl nitrobenzenes and isopropenyl nitrobenzenes were produced as side products in 5−10% yields, respectively.

Experimental Section

General Procedure. ^1H and ^{13}C NMR were measured at 270 and 67.5 MHz, respectively, in $CDCl_3$ with TMS as the internal standard. Infrared (IR) spectra were measured as thin films on NaCl plate or KBr press disk. GLC analysis was performed with a flame ionization detector with use of a 0.2 mm × 25 m capillary column (OV-1). Mass spectra were determined at an ionizing voltage of 70 eV. All starting materials, catalysts, and initiators were purchased from commercial sources and used without further treatment. NO_2 was treated as a liquid at 0 °C. *n*-Butane (**3**) and isobutane (**5**) were also treated as a liquid at −15 °C. The yields of products were estimated from the peak areas based on the internal standard technique.

All products **4**,[20] **8**,[21] **10**,[22] **18**,[23] **21**, **25**,[24] **29**,[25] **33**,[26] **37**, and **40**[27] were reported previously.

General Procedure for the Nitration of 1 or 11 with NO_2 Catalyzed by NHPI. To a 50-mL glass autoclave were added NHPI (49 mg, 0.3 mmol) and $PhCF_3$ (5 mL). Then, cooled liquid NO_2 (0.050 mL, 74 mg, 1.6 mmol) was quickly added, using a Hamilton gastight syringe and the autoclave was closed. The autoclave was pressurized to 5 atm with **1** or **11**, and the mixture was stirred at 70 °C for 14 h. After the reaction, the GC and GC-MS analyses were performed. The products were identified through a comparison of these analytical data with those of authentic samples.

General Procedure for the Nitration of 3, 5, 7, or 9 with NO_2 Catalyzed by NHPI. To a 50-mL glass autoclave were added NHPI, $PhCF_3$, and substrate. Then, NO_2 or HNO_3 was quickly added, using a Hamilton gastight syringe or glass-pipet, respectively, and the autoclave was closed. The autoclave was pressurized with air or air/nitrogen mixed gas, and the mixture was stirred at 70 °C for 14 h. The workup procedure was performed as described above.

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Procedure for the Nitration of Toluene (13) with HNO_3 Catalyzed by NHPI. To a pear-shape flask (100 mL) were added NHPI (0.2 mmol), **13** (5 mL), and *concentrated* HNO_3 (1.5 mmol). The flask was cooled to −78 °C to freeze the solvent, degassed in vacuo, and filled with Ar gas. Then the frozen solvent was melted at room temperature and refrozen to reiterate the evacuation−Ar purge procedure. The series of operations was repeated three times. The reaction mixture was allowed to react under an atmospheric pressure of Ar at 60 °C for 5 h. The workup procedure was performed as described above.

Procedure for the Nitration of Toluene (13) with NO_2 Catalyzed by NHPI. To a pear-shape flask (100 mL) were added NHPI (33 mg, 0.2 mmol) and **13** (5 mL). The flask was closed with a glass stopper and weighed. Then NO_2 (0.10 mL) was quickly added, using a Hamilton gastight syringe, and the flask was closed with the glass stopper. The flask was weighed again to measure the weight of NO_2 added. The amount of NO_2 was 150 mg (3.24 mmol). The flask was cooled in an ice-bath and then quickly attached to the condenser, and the mixture was stirred at 60 °C for 5 h. The workup procedure was performed as described above.

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