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Iron-Mediated Radical Halo-Nitration of Alkenes

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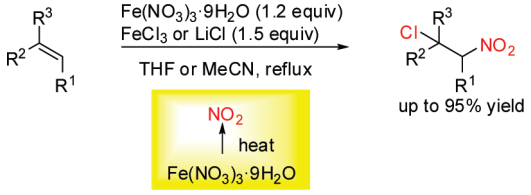
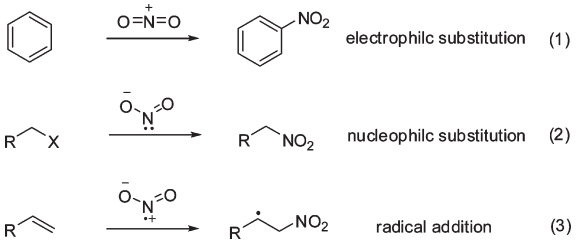


Radical halo-nitration of alkenes using iron(III) nitrate nonahydrate and halogen salt has been developed. The present reaction proceeds by radical addition of nitrogen dioxide generated by thermal decomposition of iron(III) nitrate nonahydrate and subsequent trapping of the resultant radical by a halogen atom in the presence of halogen salt. Application of this method to synthesis of nitroalkenes is also described. The practicality of the present method using nontoxic and inexpensive iron reagents has been shown by the application to broad alkenes.

Introduction

Nitro compounds are widely used in various fields such as medicine, industry, and fuels. In organic synthesis, nitro compounds are valuable synthetic intermediates because these compounds can be easily transformed into amines and ketones.[1] Classical nitration of aromatics and alkenes by electrophilic substitution using nitronium cation (NO_2^+) is well-known (Scheme 1, eq 1).[2−4] In particular, nitryl chloride (NO_2Cl) and nitrosyl chloride (NOCl) have been frequently used as a nitro group donor.[3a,b,f,l] However, nitration reactions using these reagents have drawbacks such as difficulty of handling and the limitation of substrates due to toxicity and extreme reactivity. As a method for synthesis of aliphatic nitro compounds, nucleophilic substitution reaction of an alkyl halide with nitrite anion (NO_2^-) has been used (Scheme 1, eq 2).[5] Oxidation of amines and oximes also affords corresponding nitro compounds.[6] Recently, Fors and Buchwald have reported palladium-catalyzed synthesis of nitroaromatics from aryl chlorides, triflates, and nonaflates using sodium nitrite.[7] On the other hand, nitrogen dioxide gas (NO_2), which is a free radical, is one of the simplest and most common nitration reagents.[8] Addition of nitrogen dioxide to a C−C multiple bond easily affords aliphatic nitro compounds (Scheme 1, eq 3).[9,10] However, this method has serious

SCHEME 1. Methods of Nitration



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(2) For reviews on nitration of aromatic compounds, see: (a) Olah, G. A.; Malhotra, R.; Narang, S. C. *Nitration: Methods and Mechanisms*; VCH Publishers Inc.: New York, 1989. (b) Suzuki, T.; Noyori, R. *Chemtracts* **1997**, *10*, 813.

(3) For examples of nitration of alkenes, see: (a) Shechter, H.; Conrad, F.; Daulton, A. L.; Kaplan, R. B. *J. Am. Chem. Soc.* **1952**, *74*, 3052. (b) Terada, A.; Hassner, A. *Bull. Chem. Soc. Jpn.* **1967**, *40*, 1937. (c) Bachman, G. B.; Whitehouse, M. L. *J. Org. Chem.* **1967**, *32*, 2303. (d) Corey, E. J.; Estreicher, H. *J. Am. Chem. Soc.* **1978**, *100*, 6294. (e) Hayama, T.; Tomoda, S.; Takeuchi, Y.; Nomura, Y. *Tetrahedron Lett.* **1982**, *23*, 4733. (f) Jew, S.-S.; Kim, H.-D.; Cho, Y.-S.; Cook, C.-H. *Chem. Lett.* **1986**, 1747. (g) Butts, C. P.; Calvert, J. L.; Eberson, L.; Hartshorn, M. P.; Robinson, W. T. *J. Chem. Soc., Perkin Trans. 2* **1994**, 1485. (h) Hata, E.; Yanada, T.; Mukaiyama, T. *Bull. Chem. Soc. Jpn.* **1995**, *68*, 3629. (i) Campos, P. J.; García, B.; Rodríguez, M. A. *Tetrahedron Lett.* **2000**, *41*, 979. (j) Stepanov, A. V.; Veselovsky, V. V. *Russ. Chem. Rev.* **2003**, *72*, 327. (k) Jovel, I.; Prateeptongkum, S.; Jackstell, R.; Vogl, N.; Weckbecker, C.; Beller, M. *Adv. Synth. Catal.* **2008**, *350*, 2493. (l) Sprecher, H.; Pletscher, S.; Möri, M.; Marti, R. *Helv. Chim. Acta* **2010**, *93*, 90. See also refs 9 and 10.

(4) Olah and co-workers have also reported a direct nitration of alkane using nitronium tetrafluoroborate; see: Olah, G. A.; Ramaiah, P.; Rao, C. B.; Graham, S.; Golam, R.; Trivedi, N. J.; Olah, J. A. *J. Am. Chem. Soc.* **1993**, *115*, 7246.

(5) (a) Kornblum, N.; Taub, B.; Ungnade, H. E. *J. Am. Chem. Soc.* **1954**, *76*, 3209. (b) Kornblum, N.; Powers, J. W. *J. Org. Chem.* **1957**, *22*, 455.

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drawbacks such as the difficulty of handling NO_2 gas and its toxicity. Therefore, the reaction using nitrogen dioxide is used in limited cases of synthetic chemistry.

It is well-known that thermal decomposition of iron(III) nitrate nonahydrate, $Fe(NO_3)_3 \cdot 9H_2O$, generates nitrogen dioxide (NO_2),[11,12] but synthetic applications of this method have never been explored. In recent years, iron compounds have become attractive as nontoxic and inexpensive green elements.[13] Many chemists have shown interest in iron complexes as replacements for expensive transition metal catalysts such as palladium and rhodium for carbon−carbon or carbon−heteroatom bond formation.[14] Recently, we reported iron-mediated radical nitro-cyclization of 1,6-dienes **1** to give five-membered compounds **2** bearing a nitro group by sequential steps that involved radical addition of nitrogen dioxide to 1,6-dienes promoted by the thermal decomposition of iron(III) nitrate nonahydrate, cyclization, and trapping of the resultant terminal radicals by a halogen atom in the presence of halogen salt (Scheme 2).[15] It is expected that radical nitration of alkenes using $Fe(NO_3)_3 \cdot 9H_2O$ will provide a general and practical method for the synthesis of nitro compounds from the viewpoints of safety and economy. In this paper, we present a full account of this work including extension to nitration reactions of various alkenes.

SCHEME 2. Radical Nitro-Cyclization of 1,6-Dienes

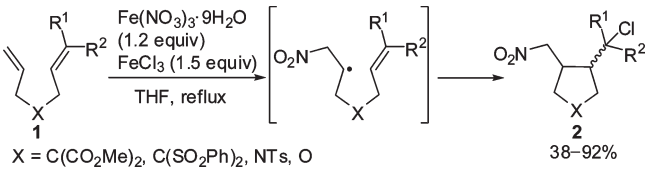
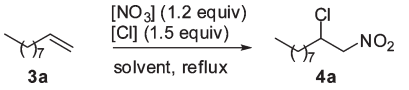


TABLE 1. Chloro-Nitration of Decene (3a)



entry	NO_3	Cl	solvent	time (h)	yield (%)
1	$Fe(NO_3)_3 \cdot 9H_2O$	$FeCl_3$	THF	2	77
2	$Fe(NO_3)_3 \cdot 9H_2O$	$FeCl_3$	MeCN	1	84
3	$Fe(NO_3)_3 \cdot 9H_2O$	LiCl	MeCN	5	71
4[a]	$LiNO_3$	$FeCl_3$	MeCN	4	61

[a] 5 equiv of $LiNO_3$ and 2 equiv of $FeCl_3$ were employed.

Results and Discussion

In our previous study, reaction conditions using several nitrate and chloride salts were examined, and the results indicated that a combination of $Fe(NO_3)_3 \cdot 9H_2O/FeCl_3$ in boiling THF was the best condition.[15] First, we examined the application of these reaction conditions to simple alkenes. Treatment of decene (**3a**) under similar conditions ($Fe(NO_3)_3 \cdot 9H_2O/FeCl_3$ in boiling THF) gave 2-chloro-1-nitrodecane (**4a**) in good yield (Table 1, entry 1). We found that using MeCN instead of THF as a solvent resulted in slight improvement in yield with shorter reaction time (Table 1, entry 2). Using LiCl as a chlorine source and $LiNO_3$ as a nitrate source in the presence of iron also gave nitrated compound **4a** in slightly lower yields than in the case of conditions of entry 2 (Table 1, entries 3 and 4).

Iron-mediated chloro-nitration of various alkenes is shown in Table 2. The nitration reactions of allylamine derivative **3b** and 2,2-disubstitute alkene **3c** gave chloro-nitrated compounds **4b** and **4c**, respectively, in good yields (Table 2, entries 1 and 2). The reaction using styrene (**3d**) as a substrate also readily proceeded to give 2-chloro-1-nitro-3-phenylethane (**4d**) in good yield along with a small amount of eliminated product **4d′**. When the reaction of α-methylstyrene (**3e**) was performed with $Fe(NO_3)_3 \cdot 9H_2O/FeCl_3$ in MeCN, polymerization and nitration of the aromatic ring probably competed to give a complex mixture. However, we soon found that using LiCl instead of $FeCl_3$ gave the desired chloro-nitrated product **4e** in moderate yield along with a small amount of eliminated product **4e′** (Table 2, entry 5). The present reaction might have milder reactivity with the use of LiCl, which is a weak Lewis base, rather than $FeCl_3$, which is a strong Lewis acid. Thus, this result shows that the scope of the present reaction allows for extension by using LiCl as a chlorine source. *p*-Bromo-α-methylstyrene (**3f**) gave a chloro-nitrated product (**4f**) with a small amount of eliminated product (**4f′**) under the condition of use of $FeCl_3$ (Table 2, entry 6). The reaction of *p*-nitro-α-methylstyrene (**3g**) with $Fe(NO_3)_3 \cdot 9H_2O/FeCl_3$ readily proceeded to give chloro-nitrated product **4g** in high yield (Table 2, entry 7). This high yield can be attributed to restraint of side reactions such as polymerization and nitration

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(8) (a) Mori, T.; Suzuki, H. *Synlett* **1995**, 383. (b) Suzuki, H.; Nonoyama, N. *J. Chem. Soc., Chem. Commun.* **1996**, 1783. (c) Nishiwaki, Y.; Sakaguchi, S.; Ishii, Y. *J. Org. Chem.* **2002**, *67*, 5663.

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(10) Radical nitration of styrene derivatives using cerium(IV) ammonium nitrate and sodium nitrite has been reported; see: (a) Hwu, J. R.; Chen, K.-L.; Ananthan, S.; Patel, H. V. *Organometallics* **1996**, *15*, 499. (b) Grenier, J.-L.; Catteau, J.-P.; Cotelle, P. *Synth. Commun.* **1999**, *29*, 1201. (c) Jayakanthan, K.; Madhusudanan, K. P.; Vankar, Y. D. *Tetrahedron* **2004**, *60*, 397.

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(12) The synthesis of azides from hydrazines using nitrogen dioxide generated from clay-supported $Fe(NO_3)_3$ (clayfen) has been reported; see: (a) Laszlo, P.; Polla, E. *Tetrahedron Lett.* **1984**, *25*, 3701. The synthesis of β-nitrostyrenes using clayfen has been also reported: (b) Verma, R. S.; Naicker, K. P.; Liesen, P. J. *Tetrahedron Lett.* **1998**, *39*, 3977.

(13) For reviews on iron-catalyzed reactions, see: (a) *Iron Catalysis in Organic Chemistry*; Plietker, B., Ed.; Wiley-VCH: Weinheim, 2008. (b) Bolm, C.; Legros, J.; Le Paih, J.; Zani, L. *Chem. Rev.* **2004**, *104*, 6217. (c) Correa, A.; García Mancheño, O.; Bolm, C. *Chem. Soc. Rev.* **2008**, *37*, 1108. (d) Enthaler, S.; Junge, K.; Beller, M. *Angew. Chem., Int. Ed.* **2008**, *47*, 3317. (e) Sherry, B. D.; Fürstner, A. *Acc. Chem. Res.* **2008**, *47*, 1500. (f) Correa, A.; García Mancheño, O.; Bolm, C. *Chem. Soc. Rev.* **2008**, *37*, 1108. (g) Fürstner, A. *Angew. Chem., Int. Ed.* **2009**, *48*, 1364. (h) Sarhan, A. A.; Bolm, C. *Chem. Soc. Rev.* **2009**, *38*, 2730.

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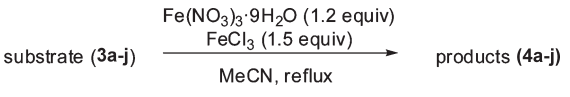
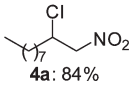
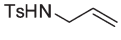
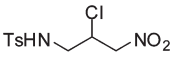
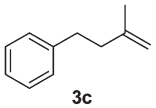
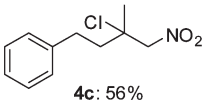
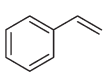
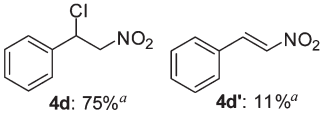
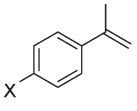
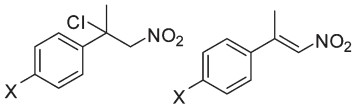
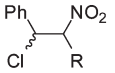
TABLE 2. Chloro-Nitration of Various Alkenes



entry	substrate	time (h)	products
1	 **3a**	1	 **4a**: 84%
2	 **3b**	5	 **4b**: 95%
3	 **3c**	0.5	 **4c**: 56%
4	 **3d**	3	 **4d**: 75%[a] **4d'**: 11%[a]
5[b]	 **3e**: X = H	5	 **4e**: 54%[a] **4e'**: 9%[a]
6	**3f**: X = Br	0.5	**4f**: 49%[a] **4f'**: 8%[a]
7	**3g**: X = NO_2	4	**4g**: 80% **4g'**: not detected
8	**3h**: X = OMe	0.5	complex mixture
9	 **3i**: R = Me	0.5	 **4i**: 80% (53:47)[c]
10	**3j**: R = Ph	3	**4j**: 11%

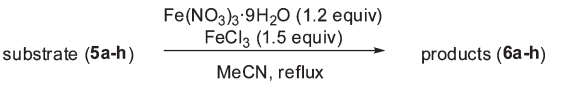
[a]Yield was determined by ^{1}H NMR analysis. [b]LiCl was employed instead of $FeCl_3$. [c]Diastereomeric ratio was determined by ^{1}H NMR analysis.

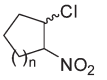
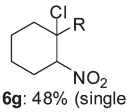
of the aromatic ring because of the electron-deficient effect of the *p*-nitrophenyl group. On the other hand, the reaction of electron-rich *p*-methoxy-α-methylstyrene (**3h**) gave a complex mixture, even when the reaction was carried out under the condition of use of LiCl (Table 2, entry 8). *trans*-*β*-Methylstyrene (**3i**) readily underwent chloro-nitration reaction to give 3-chloro-2-nitro-3-phenylpropane (**4i**) in good yield (Table 2, entry 9), whereas *trans*-stilbene (**3j**) gave 1-nitro-1,2-diphenylethane (**4j**) in very low yield (Table 2, entry 10). As in the reactions of **3e** and **3h**, it is assumed that side reactions such as polymerization and nitration of the aromatic ring competed in the reaction of **4j**.

Subsequently, chloro-nitration reactions of cyclic alkenes were examined (Table 3). Treatment of five-, six-, seven-, eight-, and twelve-membered cycloalkenes **5a**−**e** with $Fe(NO_3)_3 \cdot 9H_2O/FeCl_3$ in MeCN afforded the corresponding 2-chloro-1-nitro cycloalkanes **6a**−**e** in good yields (Table 3, entries 1−5). On the other hand, low reactivity of norbornene (**5f**) was observed (Table 3, entry 6). The reaction of trisubstituted cycloalkenes **5g** and **5h** gave chloro-nitrated products **6g** and **6h**, respectively, in moderate yields (Table 3, entries 7 and 8).

Reactions using electron-deficient alkenes as substrates were also examined (Table 4). Treatment of ethyl acrylate

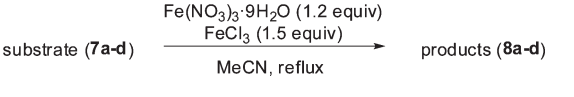
TABLE 3. Chloro-Nitration of Cyclic Alkenes

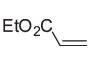
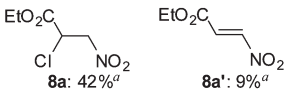
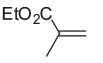
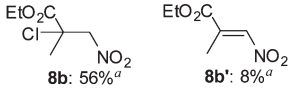
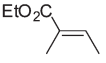
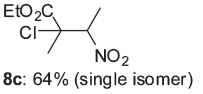
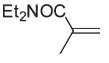
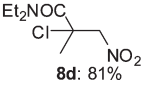


entry	substrate	time (h)	products[a]
1	 **5a**: n = 1	3	 **6a**: 71% (87:13)
2	**5b**: n = 2	3	**6b**: 74% (72:28)
3	**5c**: n = 3	3	**6c**: 91% (87:13)
4	**5d**: n = 4	3	**6d**: 88% (82:18)
5[b]	**5e**: n = 8	2	**6e**: 78% (72:28)
6	 **5f**	4	 **6f**: 35% (67:33)
7[c]	 **5g**: R = Me	4	 **6g**: 48% (single isomer)
8[c]	**5h**: R = Ph	0.25	**6h**: 65% (single isomer)

[a]Diastereomeric ratio was determined by ^{1}H NMR analysis (*trans* isomer is major). [b]**5e** was used as a mixture of *trans* and *cis* isomers. [c]LiCl was employed instead of $FeCl_3$.

TABLE 4. Chloro-Nitration of Electron-Deficient Alkenes

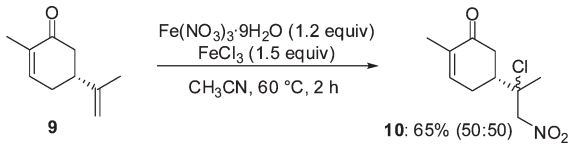


entry	substrate	time (h)	product
1	 **7a**	9	 **8a**: 42%[a] **8a'**: 9%[a]
2	 **7b**	5	 **8b**: 56%[a] **8b'**: 8%[a]
3	 **7c**	8	 **8c**: 64% (single isomer)
4	 **7d**	4	 **8d**: 81%

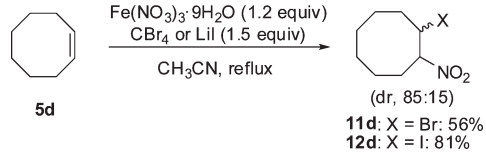
[a]Yield was determined by ^{1}H NMR analysis.

(**7a**) and ethyl methacrylate (**7b**) with $Fe(NO_3)_3 \cdot 9H_2O/FeCl_3$ in MeCN afforded nitrated ethyl esters **8a** and **8b** in moderate yield along with small amounts of eliminated products **8a**′ and **8b**′, respectively (Table 4, entries 1 and 2). The reaction of ethyl tiglate (**7c**) gave nitrated product **8c** as a single diastereomer (Table 4, entry 3). The reaction of methacrylamide **7d** successfully proceeded to give 2-chloro-3-nitropropionamide **8c** in good yields (Table 4, entry 4). When the reaction of *β*-carvone (**9**) bearing electron-rich and deficient alkene moieties in the molecule was carried out at a lower temperature (60 °C), selective addition of a nitro group to electron-rich

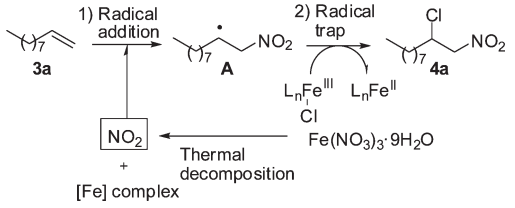
SCHEME 3. Chemoselective Chloro-Nitration of β-Carvone (9)



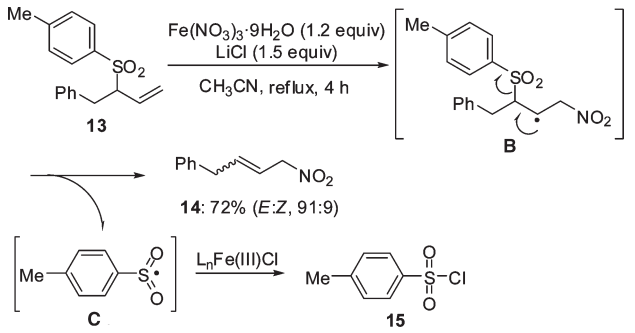
SCHEME 4. Radical Trap by Other Halogen Atoms



SCHEME 5. Plausible Reaction Mechanism



SCHEME 6. Radical Nitration of Compound 13



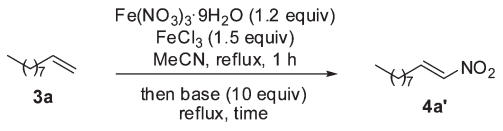
alkene occurred to give mononitrated compound **10** in good yield (Scheme 3).

Brominated or iodinated compounds were also accessible by using appropriate radical trapping reagents. In the reaction of 1,6-diene, we found that treatment of 1,6-diene with $Fe(NO_3)_3 \cdot 9H_2O$ in the presence of carbon tetrabromide or lithium iodide afforded brominated or iodinated products, respectively.[15] The reaction of cyclooctene (**5d**) was performed under similar conditions to give brominated and iodinated products **11d** and **12d** in moderate and good yields, respectively (Scheme 4).

A plausible mechanism for the chloro-nitration reaction is shown in Scheme 5. For the reaction of simple alkene **3a**, addition of nitrogen dioxide (NO_2), generated by thermal decomposition of $Fe(NO_3)_3 \cdot 9H_2O$, onto **3a** takes place to give radical intermediate **A**. The radical intermediate **A** is then trapped by a chlorine atom from the iron chloride complex to give **4a**. Although the possibility that the formation of **4a** involves oxidation of the radical intermediate **A** followed by addition of chloride anion to the resultant cation intermediate as another path cannot be ruled out, the main path would be the direct radical trapping mechanism by a chlorine atom because the reactions of α,β-unsaturated esters **7a**−**c** and amide **7d** also proceeded (Table 4). In order to obtain evidence of a radical mechanism, the reaction of allylsulfonyl derivative **13** was examined. Treatment of **13** with $Fe(NO_3)_3 \cdot 9H_2O$ in the presence of LiCl in MeCN resulted in elimination of the sulfonyl group to give nitro compound **14** in good yield with detection of *p*-toluenesulfonyl chloride **15** (Scheme 6). This result provides support for the generation of radical intermediate **B** followed by elimination of a stable sulfonyl radical **C**, which abstracted a chlorine atom from the iron complex to give *p*-toluenesulfonyl chloride.[16,17]

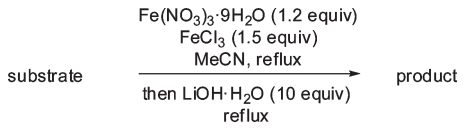
Finally, one-pot synthesis of useful nitroalkenes using this iron-mediated nitration reaction was examined.[18] After decene (**3a**) had been treated with $Fe(NO_3)_3 \cdot 9H_2O/FeCl_3$ in boiling MeCN, addition of Et_3N to the reaction mixture afforded a complex mixture (Table 5, entry 1). However, we soon found that using K_2CO_3 instead of Et_3N gave desired

TABLE 5. One-Pot Synthesis of Nitroalkene 4a



entry	base	time (h)	yield (%)
1	Et_3N	1	complex mixture
2	K_2CO_3	0.5	15
3	$LiOH \cdot H_2O$	0.5	82

TABLE 6. One-Pot Synthesis of Several Nitroalkenes



entry	substrate	time (h)	product
1	**3a**	1 + 0.5	**4a'**: 82%
2	**3d**	3 + 0.25	**4d'**: 66%
3	**5d**	3 + 3	**6d'**: 62%
4	**5e**	2 + 3	**6e'**: 56%

(16) Guyader, F. L.; Quiclet-Sire, B.; Seguin, S.; Zard, S. Z. *J. Am. Chem. Soc.* **1997**, *119*, 7410.

(17) In order to obtain evidence of the radical mechanism, *trans*-1-phenyl-2-vinylcyclopropane was employed as a radical clock, but the decomposition of substrate or product was observed in the reaction of this compound.

(18) For reviews on nitroalkenes, see: (a) Barret, A. G. M.; Graboski, G. G. *Chem. Rev.* **1986**, *86*, 751. (b) Ballini, R.; Marcantoni, E.; Petrini, M. In *Amino Group Chemistry*; Ricci, A., Ed.; Wiley-VCH: New York, 2008; pp 93−148. See also ref 2 1, 3, 9, and 10.

nitroalkene **4a′** in one pot (Table 5, entry 2). Eventually, the use of $LiOH \cdot H_2O$ as a base significantly improved the yield of the product (Table 5, entry 3). As shown in Table 6, styrene (**3d**) and cycloalkene **5d** and **5e** also readily underwent the one-pot chloro-nitration/elimination process to give nitroalkenes **4d′**, **6d′**, and **6e′**, respectively, in good yields.

Conclusions

In conclusion, we have developed an iron-mediated nitration reaction of alkenes to give halo-nitro compounds. In the present reaction, a radical mechanism was suggested by investigation of nitro-cyclization of 1,6-dienes, and this reaction was extended to halo-nitration of various alkenes. Furthermore, one-pot synthesis of synthetic valuable nitroalkene using this method was shown. The present reaction has large advantages such as the simple and safe experimental procedure using nontoxic and inexpensive reagents. Therefore, the present reaction will provide a general and practical method for the synthesis of nitro compounds.

Experimental Section

General. All reactions were carried out in flame-dried glassware under nitrogen atmosphere. All reagents were purchased commercially and used without further purification. Melting points are uncorrected. IR spectra were recorded on a commercial FT/IR spectrometer. ^{1}H NMR spectra were recorded at 600, 500, and 400 MHz; chemical shifts (δ) are quoted relative to tetramethylsilane. ^{13}C NMR spectra were recorded at 150, 125, and 100 MHz with complete proton decoupling; chemical shift (δ) are quoted relative to the residual signals of chloroform. Silica gel column chromatography was carried out on silica gel 60N. Mass spectra were recorded on a high-resolution mass spectrometer in fast atom bombardment mode (FAB).

Starting Materials. Compounds **3a**, **3d**, **3e**, **3i**, **3j**, **5a**−**h**, **7a**−**c**, and **9** were commercially available. Compound **3b**[19] was prepared by N-tosylation of allylamine. Compounds **3c**,[20] **3f**,[21] **3g**,[22] and **3h**[21] were prepared by Wittig reaction of corresponding commercially available ketones. Compound **7d**[23] was prepared by acylation of diethylamine with methacryloyl chloride. Compound **13**[24] was prepared according to literature.

Typical Procedure of Halo-Nitration of Alkenes. To a solution of **3a** (74.1 mg, 0.528 mmol) and $FeCl_3$ (256 mg, 0.792 mmol) in CH_3CN (2.6 mL) was added $Fe(NO_3)_3 \cdot 9H_2O$ (128 mg, 0.634 mmol), and the mixture was heated at reflux for 1 h. After cooling to room temperature, the resulting suspension was diluted with Et_2O and filtered. After removal of solvent under reduced pressure, the residue was purified by chromatography (hexane/EtOAc, 10:1) to give **4a** (97.8 mg, 84%) as a colorless oil.

2-Chloro-1-nitrodecane (4a). 84% yield. Colorless oil. IR ($CHCl_3$) υ 1562, 1379, 1225 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.89 (3H, t, J = 6.9 Hz), 1.24−1.42 (10H, br), 1.48−1.58 (2H, m), 1.74−1.81(2H, m), 4.50−4.55 (1H, m), 4.58 (1H, d, J = 1.8 Hz), 4.60 (1H, m); ^{13}C NMR (150 MHz, $CDCl_3$) δ 14.1, 22.6, 25.8, 28.8, 29.1, 29.3, 31.8, 35.0, 56.2, 80.5; HRFABMS calcd for $C_{10}H_{21}ClNO_2$ ($M^+ + H$) 222.1261, found 222.1264.

***N*-(2-Chloro-3-nitropropyl)toluenesulfonamide (4b).** 95% yield. Colorless crystals, mp 68.0−68.5 °C. IR ($CHCl_3$) υ 1563, 1337, 1223, 1163 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.45 (3H, s), 3.32−3.46 (2H, m), 4.56−4.62 (1H, m), 4.70 (1H, dd, J = 14.1, 7.5 Hz), 4.81 (1H, dd, J = 13.9, 4.9 Hz), 4.96 (1H, t, J = 7.1 Hz), 7.35 (2H, d, J = 8.0 Hz), 7.74 (2H, d, J = 8.3 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.5, 46.2, 54.1, 77.3, 127.0, 130.1, 136.1, 144.4. Anal. Calcd for $C_{10}H_{13}ClN_2O_4S$: C, 41.03; H, 4.48; N, 9.57. Found: C, 40.90; H, 4.34; N, 9.55.

2-Chloro-2-methyl-1-nitro-4-phenylbutane (4c). 56% yield. Colorless oil. IR ($CHCl_3$) υ 1556, 1456, 1375 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.80 (3H, s), 2.20 (2H, m), 2.87 (2H, td, J = 9.3, 7.3 Hz), 4.67 (1H, d, J = 17.2 Hz), 4.74 (1H, d, J = 17.2 Hz), 7.20−7.32 (5H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 28.5, 30.8, 43.6, 66.8, 84.0, 126.4, 128.4, 128.6, 140.3; HRFABMS calcd for $C_{11}H_{15}ClNO_2$ (M^++H) 228.0791, found 228.0799.

1-Chloro-2-nitro-1-phenylethane (4d) and 1-Nitro-2-phenylethene (4d′).[25] 75% (**4d**) and 11% (**4d′**) yields (**4d** and **4d′** were isolated as an inseparable mixture). Colorless oil. IR ($CHCl_3$) υ 1564, 1377, 1346 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, for **4d** including the partial peaks of **4d′**) δ 4.77 (1H, dd, J = 13.7, 5.5 Hz), 4.90 (1H, dd, J = 13.7, 9.2 Hz), 5.56 (1H, dd, J = 9.1, 5.5 Hz), 7.38−7.60 (11H, m, for **4d** and **4d′**), 8.00 (1H, d, J = 13.7 Hz, for **4d′**); ^{13}C NMR (100 MHz, $CDCl_3$, for **4d** including the peaks of **4d′**) δ 56.8, 80.7, 127.1, 129.1 (**4d′**), 129.2, 129.3 (**4d′**), 129.7, 130.0 (**4d′**), 132.1 (**4d′**), 135.7, 137.0 (**4d′**), 139.1(**4d′**); HRFABMS (for **4d**) calcd for $C_8H_9ClNO_2$ (M^+ + H) 186.0322, found 186.0320. HRFABMS (for **4d′**) calcd for $C_8H_9NO_2$ (M^+ + H) 150.0555, found 150.0555.

2-Chloro-1-nitro-2-phenylpropane (4e) and 1-Nitro-2-phenylpropene (4e′).[21] 54% (**4e**) and 9% (**4e′**) yields (**4e** and **4e′** were isolated as an inseparable mixture). Colorless oil. IR ($CHCl_3$) υ 1558, 1448, 1373, 1269 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, for **4e** including the partial peaks of **4e′**) δ 2.23 (3H, s), 2.64 (3H, s, for **4e′**), 4.90 (1H, d, J = 11.7 Hz), 4.93 (1H, d, J = 11.7 Hz), 7.26−7.45 and 7.55−7.59 (total 11H, m, for **4e** and **4e′**), (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$, for **4e** including the partial peaks of **4e′**) δ 18.6 (**4e′**), 29.0, 66.9, 86.0, 126.1, 128.8, 128.9, 130.3 (**4e′**), 136.3 (**4e′**), 138.2 (**4e′**), 140.0, 150.0 (**4e′**); HRFABMS (for **4e**) calcd for $C_9H_{11}ClNO_2$ (M^+ + H) 200.0478, found 200.0483. HRFABMS (for **4e′**) calcd for $C_9H_{11}NO_2$ (M^+ + H) 164.0712, found 164.0711.

2-(4-Bromophenyl)-2-chloro-1-nitropropane (4f) and 2-(4-Bromophenyl)-1-nitropropene (4f′).[21] 49% (**4f**) and 8% (**4f′**) yields (**4f** and **4f′** were isolated as an inseparable mixture). Colorless oil. IR ($CHCl_3$) υ 1560, 1490, 1342 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$, for **4f** including the peaks of **4f′**) δ 2.20 (3H, s), 2.64 (3H, d, J = 1.4 Hz, for **4f′**) 4.82 (1H, d, J = 11.9 Hz), 4.93 (1H, d, J = 11.9 Hz), 7.29 (1H, d, J = 1.4 Hz, for **4f′**), 7.33 (2H, d-like, J = 8.2 Hz, for **4f′**), 7.43 (2H, d-like, J = 8.2 Hz), 7.54 (2H, d-like, J = 8.2 Hz), 7.58 (2H, d-like, J = 8.2 Hz, for **4f′**); ^{13}C NMR (150 MHz, $CDCl_3$, for **4f** including the peaks of **4f′**) δ 18.4 (**4f′**), 29.0, 66.2, 85.6, 123.3, 127.9, 128.3 (**4f′**), 131.8 (**4f′**), 131.9, 132.3 (**4f′**), 136.4 (**4f′**), 137.1 (**4f′**), 139.1, 148.6 (**4f′**); HRFABMS (for **4f**) calcd for $C_9H_{10}ClO_2NBr$ (M^+ + H) 277.9583, found 277.9597. HRFABMS (for **4f′**) calcd for $C_9H_9O_2BrN$ (M^++H) 241.9817, found 241.9818.

2-Chloro-1-nitro-2-(4-nitrophenyl)propane (4g). 80% yield. Colorless crystals, mp 68.0−68.5 °C (hexane/EtOAc). IR ($CHCl_3$) υ 1560, 1529, 1371, 1350 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.25 (3H, s), 4.96 (1H, d, J = 12.4 Hz), 5.01 (1H, d, J = 12.4 Hz) 7.76 (2H, d, J = 8.9 Hz), 8.27 (2H, d, J = 8.9 Hz); ^{13}C NMR (150 MHz, $CDCl_3$) δ 29.3, 65.6, 85.3, 123.9, 127.5, 146.8, 147.9. Anal. Calcd for $C_9H_9ClN_2O_4$: C, 44.19; H, 3.71; N, 11.45. Found: C, 44.44; H, 3.66; N, 11.47.

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(25) Black, P.-J.; Gerta, C.-K.; Edwards, M. G.; Slatford, P. A.; Whittlesey, M. K.; Williams, J. M. J. *Org. Biomol. Chem.* **2006**, *4*, 116.

1-Chloro-2-nitro-1-phenylpropane (4i). 80% yield. Colorless oil. (**4i** was an inseparable mixture of two isomers, 53:47). IR ($CHCl_3$) υ 1560, 1454, 1389, 1360 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, for a mixture of two isomers) δ 1.35 (3H, d, $J = 6.8$ Hz), 1.71 (3H, d, $J = 6.6$ Hz), 4.93 (1H, dq, $J = 9.6$, 6.9 Hz), 5.01 (1H, dq, $J = 7.3$, 6.9 Hz), 5.22 (1H, d, $J = 10.3$ Hz), 5.38 (1H, d, $J = 7.6$ Hz), 7.35−7.42 (10H, m); ^{13}C NMR (150 MHz, $CDCl_3$, for a mixture of two isomers) δ 15.7, 17.9, 62.3, 62.6, 87.5, 88.9, 127.4, 127.8, 128.9, 129.2, 129.4, 129.7, 135.5, 136.2; HRFABMS calcd for $C_9H_{11}ClNO_2$ ($M^+ + H$) 200.0478, found 200.0479.

1-Chloro-1,2-diphenyl-2-nitroethane (4j). 11% yield. Colorless oil. IR ($CHCl_3$) υ 1655, 1562, 1522, 1325, 1277 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 5.73 (1H, d, $J = 11.0$ Hz), 5.87 (1H, d, $J = 11.0$ Hz), 7.21−7.29 (10H, m); ^{13}C NMR (150 MHz, $CDCl_3$) δ 61.9, 96.7, 127.88, 127.93, 128.8, 129.0, 130.3, 135.1; HRFABMS calcd for $C_{14}H_{12}ClNO_2$ ($M^+ + H$) 262.0636, found 262.0635.

1-Chloro-2-nitrocyclopentane (6a). 71% yield (as a separable mixture of two isomers, 87:13). Major isomer: colorless oil. IR ($CHCl_3$) υ 1552, 1371 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 1.94−2.05 (3H, m), 2.25−2.30 (1H, m), 2.37−2.43 (1H, m), 2.49 (1H, td, $J = 14.4$, 8.2 Hz), 4.72−4.75 (1H, m), 4.96 (1H, dt, J = 8.2, 3.4 Hz); ^{13}C NMR (150 MHz, $CDCl_3$) δ 22.3, 30.4, 35.3, 60.4, 93.0; HRFABMS calcd for $C_5H_9ClNO_2$ ($M^+ + H$) 150.0322, found 150.0328. Minor isomer: colorless oil. IR ($CHCl_3$) υ 1556, 1375, 1219 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.76−1.84 (1H, m), 2.16−2.25 (4H, m), 2.53−2.65 (11H, m), 4.55 (1H, dd, $J = 10.5$, 5.5 Hz) 4.98 (1H, td, $J = 7.3$, 5.5 Hz); ^{13}C NMR (150 MHz, $CDCl_3$) 20.5, 26.2, 33.6, 59.5, 88.9; HRFABMS calcd for $C_5H_9ClNO_2$ ($M^+ + H$) 150.0322, found 150.0325.

1-Chloro-2-nitrocyclohexane (6b).[26] 74% yield (as a separable mixture of two isomers, 72:28). Major isomer: colorless oil. IR ($CHCl_3$) υ 1562, 1453, 1374, 1225 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.36−1.45 (2H, m), 1.64−1.75 (1H, m), 1.82−1.94 (3H, m), 2.33−2.42 (2H, m), 4.29 (1H, td, $J = 11.0$, 4.6 Hz), 4.51 (1H, td, $J = 11.4$, 4.6 Hz); ^{13}C NMR (150 MHz, $CDCl_3$) δ 23.4, 24.8, 31.9, 34.7, 57.7, 91.5.; HRFABMS calcd for $C_6H_{11}ClO_2N$ ($M^+ + H$) 164.0478, found 164.0476. Minor isomer: colorless oil. IR ($CHCl_3$) υ 1552, 1377, 1221 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.25−1.38 (1H, m), 1.54−1.60 (1H, m), 1.68−1.81 (1H, m), 1.84−1.98 (2H, m), 2.13−2.31 (3H, m), 4.47 (1H, dt, $J = 11.4$, 4.1 Hz), 4.97 (1H, br); ^{13}C NMR (150 MHz, $CDCl_3$) δ 18.7, 23.3, 23.4, 32.9, 58.2, 85.4; HRFABMS calcd for $C_6H_{11}ClNO_2$ ($M^+ + H$) 164.0478, found 164.0476.

1-Chloro-2-nitrocycloheptane (6c). 91% yield. (as an inseparable mixture of two isomers, 87:13). Colorless oil. IR ($CHCl_3$) υ 1557, 1458, 1377 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$, including the partial peaks of minor isomer) δ 1.60−1.65 (4H, m), 1.81−1.89 (2H, m), 1.98−2.05 (1H, m), 2.06−2.12 (1H, m), 2.15−2.20 (1H, m), 2.24−2.29 (1H, m), 2.29−2.39 (2H, m, for minor isomer), 4.58 (1H, td, $J = 8.9$, 3.4 Hz), 4.62 (1H, dt, J = 11.0, 4.1 Hz, for minor isomer), 4.69 (1H, td, $J = 8.9$, 3.4 Hz), 4.98 (1H, m, for minor isomer); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.2 (minor), 22.8 (minor), 23.6, 23.6, 25.9 (minor), 26.2 (minor), 27.1, 31.5, 34.1 (minor), 34.8, 60.9, 61.3 (minor), 89.7 (minor), 95.2; HRFABMS calcd for $C_7H_{13}ClNO_2$ ($M^+ + H$) 178.0635, found 178.0640.

1-Chloro-2-nitrocyclooctane (6d). 88% yield (as an inseparable mixture of two isomers, 82:18). Colorless oil. IR ($CHCl_3$) υ 1556, 1466, 1381, 1223 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$, including the partial peaks of minor isomer) δ 1.34−1.52 (2H, m), 1.60−1.73 (5H, m), 1.79−1.92 (2H, m), 2.05−2.19 (2H, m), 2.26−2.32 (1H, m), 4.72 (1H, ddd, J = 10.3, 6.9, 2.7 Hz), 4.79−4.84 (1H, m, for minor isomer) 4.84−4.88 (1H, ddd, $J = 10.3$, 7.6, 2.1 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.9 (minor), 23.3, 24.5, 24.8 (minor), 24.97 (minor), 24.99 (minor), 25.4, 26.6, 27.1 (minor), 31.1, 31.3, 33.5 (minor), 60.9, 61.1 (minor), 88.3 (minor), 94.0; HRFABMS calcd for $C_8H_{15}ClNO_2$ ($M^+ + H$) 192.0791, found 192.0796.

1-Chloro-2-nitrocyclododecene (6e). 78% yield (as an inseparable mixture of two isomers, 72:28). Colorless oil. IR ($CHCl_3$) υ 1558, 1470, 1371 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$, including the partial peaks of minor isomer) δ 1.29−1.51 (15H, m), 1.72−1.78 (1H, m), 1.82−1.87 (1H, m), 1.93−2.04 (3H, m), 4.47 (1H, dt, $J = 14.4$, 4.1 Hz), 4.57 (1H, br, minor isomer), 4.73 (1H, dt, $J = 8.3$, 2.1 Hz), 4.78 (1H, ddd, $J = 10.8$, 6.1, 2.8 Hz); ^{13}C NMR (150 MHz, $CDCl_3$, including the partial peaks of minor isomer) δ 20.0, 21.4 (minor), 21.9 (minor), 22.0, 22.3 (minor), 22.4, 22.6, 22.9, 23.1, 24.4, 24.5, 24.9 (br, minor), 28.4, 30.1, 59.2, 60.3 (br, minor), 86.8 (br, minor), 90.7; HRFABMS calcd for $C_{12}H_{23}ClNO_2$ ($M^+ + H$) 248.1417, found 248.1418.

2-Chloro-3-nitrobicyclo[2.2.1]heptane (6f).[27] 35% yield (as a separable mixture of two isomers, 72:28). Major isomer: colorless oil. IR ($CHCl_3$) υ 1550, 1456, 1375 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.41−1.47 (1H, m), 1.50−1.57 (2H, m), 1.75−1.82 (1H, m), 1.84−1.86 (1H, m), 1.93−1.99 (1H, m), 2.60−2.64 (1H, m), 2.85 (1H, d, $J = 5.0$ Hz), 4.31 (1H, dd, $J = 3.6$, 2.3 Hz), 4.78 (1H, br); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.1, 26.7, 35.5, 43.3, 44.4, 61.7, 95.4; HRFABMS calcd for $C_7H_{11}ClNO_2$ ($M^+ + H$) 176.0478, found 176.0486. Minor isomer: IR ($CHCl_3$) υ 1558, 1458, 1375 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.22−1.26 (2H, m), 1.48 (1H, dt, $J = 9.6$, 1.8 Hz), 1.61−1.80 (2H, m), 2.34 (1H, dt, $J = 10.5$, 1.8 Hz), 2.55 (1H, d, $J = 4.7$ Hz), 2.88 (1H, d, $J = 3.2$ Hz), 4.24 (1H, dd, $J = 7.3$, 5.5 Hz), 4.70 (1H, dd, $J = 7.3$, 6.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 25.6, 25.9, 34.7, 41.2, 45.4, 60.4, 91.4; HRFABMS calcd for $C_7H_{11}ClNO_2$ ($M^+ + H$) 176.0478, found 176.0468.

1-Chloro-1-methyl-2-nitrocyclohexane (6g). 48% yield. Colorless oil. IR ($CHCl_3$) υ 1552, 1458, 1371 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 1.48−1.55 (1H, m), 1.56−1.63 (1H, m), 1.72 (3H, s), 1.72−1.79 (1H, m), 1.80−1.87 (1H, m), 1.95 (1H, ddd, $J = 13.7$, 9.6, 4.1 Hz), 2.06−2.13 (1H, m), 2.22−2.32 (2H, m), 4.80 (1H, dd, $J = 8.2$, 4.1 Hz); ^{13}C NMR (150 MHz, $CDCl_3$) δ 21.6, 21.9, 26.2, 27.9, 40.2, 67.5, 92.4; HRFABMS calcd for $C_7H_{13}ClNO_2$ ($M^+ + H$) 178.0635, found 178.0631.

1-Chloro-1-phenyl-2-nitrocyclohexane (6h).[28] 65% yield. Colorless crystals, mp 85.0−85.5 °C (hexane/EtOAc). IR ($CHCl_3$) υ 1552, 1448, 1378, 1296 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 1.64−1.76 (2H, m), 1.95−2.03 (2H, m), 2.26 (1H, dd, $J = 15.1$, 1.8 Hz), 2.41 (1H, br), 2.55−2.62 (1H, m), 3.10−3.18 (1H, m), 5.41 (1H, m), 7.31 (1H, t, $J = 7.6$ Hz), 7.37 (2H, t, $J = 6.9$ Hz), 7.56 (2H, d, $J = 8.3$ Hz); ^{13}C NMR (150 MHz, $CDCl_3$) δ 18.9, 20.7, 27.1, 32.1, 69.7, 89.6, 126.0, 128.6, 128.9, 141.2. Anal. Calcd for $C_{12}H_{14}ClNO_2$: C, 60.13; H, 5.89; N, 5.84. Found: C, 59.77; H, 5.72; N, 5.94.

Ethyl 2-Chloro-3-nitropropanoate (8a)[29] **and Ethyl 3-Nitroacrylate (8a′).**[29,30] 42% (**8a**) and 9% (**8a′**) yields (**8a** and **8a′** were isolated as an inseparable mixture). Colorless oil. IR ($CHCl_3$) υ 1743, 1543, 1377, 1248 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, for **8a** including the peaks of **8a′**) δ 1.34 (3H, t, $J = 6.9$ Hz), 1.37 (3H, t, $J = 6.9$ Hz, for **8a′**) 4.32 (2H, q, $J = 6.9$ Hz), 4.33 (2H, q, $J = 6.9$ Hz, for **8a′**) 4.77 (1H, dd, $J = 14.2$, 6.4 Hz), 4.88 (1H, t, $J = 6.9$ Hz), 5.00 (1H, dd, $J = 14.2$, 6.9 Hz), 7.09 (1H, d, $J = 13.1$ Hz, for **8a′**), 7.68 (1H, d, $J = 13.7$ Hz, for **8a′**); ^{13}C NMR (150 MHz, $CDCl_3$, for **8a** including the peaks of **8a′**) δ 13.8 (**8a′**), 14.0, 49.8, 62.4 (**8a′**), 63.3, 75.5, 127.7 (**8a′**), 148.9 (**8a′**), 162.6 (**8a′**), 166.2; HRFABMS calcd for $C_5H_9ClNO_4$ ($M^+ + H$) 182.0220, found 182.0218.

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Ethyl 2-Chloro-2-methyl-3-nitropropanoate (8b) and Ethyl 3-Nitromethacrylate (8b′).[3k] 56% (**8b**) and 8% (**8b′**) yields (**8b** and **8b′** were isolated as an inseparable mixture). Colorless oil. IR ($CHCl_3$) ν 1751, 1566, 1383, 1213 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, for **8b** including the peaks of **8b′**) δ 1.34 (3H, t, J = 6.9 Hz), 1.36 (3H, t, J = 6.9 Hz, for **8b′**), 1.90 (3H, s), 4.33 (2H, q, J = 7.0 Hz), 4.32 (2H, q, J = 6.9 Hz, for **8b′**), 4.84 (1H, d, J = 14.7 Hz), 5.01, (1H, d, J = 14.7 Hz), 7.73 (1H, q, J = 1.4 Hz, for **8b′**); ^{13}C NMR (150 MHz, $CDCl_3$, for **8b** including the peaks of **8b′**) δ 13.7, 13.9 (**8b′**), 25.3, 61.8 (**8b′**), 62.5 (**8b′**), 63.2, 80.9, 136.8 (**8b′**), 143.8 (**8b′**), 143.8, 165.1 (**8b′**), 168.0; HRFABMS (for **8b**) calcd for $C_6H_{11}ClO_4N$ (M^++H) 197.0455, found 197.0462. HRFABMS (for **8b′**) calcd for $C_6H_{10}NO_4$ (M^++H) 160.0610, found 160.0601.

Ethyl 2-Chloro-2-methyl-3-nitrobutanoate (8c). 64% yield. Colorless oil. IR ($CHCl_3$) ν 1751, 1556, 1456, 1392, 1298 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.31 (3H, t, J = 7.3 Hz), 1.78 (3H, d, J = 6.9 Hz), 1.88 (3H, s), 4.29 (2H, q, J = 7.3 Hz), 5.22 (1H, q, J = 7.3 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.7, 14.4, 21.9, 63.0, 65.7, 86.1, 168.4; HRFABMS calcd for $C_7H_{13}ClNO_4$ (M^+ + H) 210.0533, found 210.0539.

2-Chloro-*N*,*N*-diethyl-2-methyl-3-nitropropanamide (8d). 81% yield. Colorless oil. IR ($CHCl_3$) ν 1658, 1562, 1462, 1354 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.15 (3H, br), 1.29 (3H, br), 2.00 (3H, s), 3.37 (2H, br), 3.60 (1H, br), 3.80 (1H, br), 4.83 (1H, d, J = 13.7 Hz), 4.98 (1H, d, J = 13.7 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 12.2, 13.8, 26.4, 42.2, 42.8, 63.0, 83.1, 166.7; HRFABMS calcd for $C_8H_{16}ClN_2O_3$ (M^+ + H) 223.0850, found 223.0840.

(5*R*,7*R*)- and (5*R*,7*S*)-5-[2-Chloro-1-nitropropan-2-yl]-2-methylcyclohex-2-enone (10). 65% yield (as an inseparable mixture of two isomers, 50:50). Colorless oil. IR ($CHCl_3$) ν 1674, 1556, 1373 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$, for a mixture of two isomers) δ 1.77 (3H, s), 1.79 (3H, s), 1.80 (total 6H, two s), 2.47−2.62 (7H, m), 2.63−2.71 (2H, m), 2.78 (1H, d, J = 15.8 Hz), 4.65 (1H, d, J = 4.8 Hz), 4.68 (1H, d, J = 4.8 Hz), 4.77 (1H, d, J = 11.7 Hz), 4.81 (1H, d, J = 11.7 Hz) 6.78−6.82 (2H, m); ^{13}C NMR (150 MHz, $CDCl_3$, for a mixture of two isomers) δ 15.40, 15.42, 26.3, 26.4, 26.9, 27.1, 38.8, 39.1, 42.5, 42.6, 69.2, 69.3, 82.4, 135.4, 135.5, 143.8, 143.9, 198.1, 198.4; HRFABMS calcd for $C_{10}H_{15}ClNO_3$ (M^+ + H) 232.0741, found 232.0733.

1-Bromo-2-nitrocyclooctane (11d). 56% yield (as an inseparable mixture of two isomers, 85:15) Colorless oil. IR ($CHCl_3$) ν 1556, 1465, 1365 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$, including the partial peaks of minor isomer) δ 1.33−1.41 (1H, m), 1.43−1.51 (1H, m), 1.54−1.69 (2H, m), 1.72−1.92 (4H, m), 2.03−2.11 (1H, m), 2.13−2.20 (2H, m), 2.24−2.33 (1H, m, for minor isomer), 2.34−2.42 (1H, m), 2.45−2.51 (1H, m, for minor isomer), 4.73 (1H, dt, J = 9.6, 2.7 Hz, for minor isomer), 4.80 (1H, ddd, J = 10.3, 6.9, 2.8 Hz), 4.91−4.94 (1H, m, for minor isomer), 4.98 (1H, ddd, J = 10.7, 10.3, 2.1 Hz); ^{13}C NMR (150 MHz, $CDCl_3$) δ 24.48 (minor), 24.51, 24.7, 24.9 (minor), 25.0 (minor), 25.3, 26.5 (minor), 27.0, 27.2 (minor), 31.5, 32.1, 34.6 (minor), 52.5, 53.3 (minor), 88.3 (minor), 94.6; HRFABMS calcd for $C_8H_{15}BrNO_2$ (M^+ + H) 236.0286, found 236.0279.

1-Iodo-2-nitrocyclooctane (12d). 81% yield (as a separable mixture of two isomers, 85:15). Major isomer: colorless oil. IR ($CHCl_3$) ν 1631, 1464, 1281 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 1.31−1.42 (2H, m), 1.56−1.66 (2H, m), 1.76−1.90 (5H, m), 1.93−1.97 (1H, m), 2.05−2.18 (2H, m), 4.30 (1H, ddd, J = 9.6, 6.2, 3.4 Hz), 5.38 (1H, dt, J = 11.7, 2.2 Hz); ^{13}C NMR (150 MHz, $CDCl_3$) δ 24.9, 25.0, 26.5, 26.6, 31.6, 31.9, 32.0, 90.4; HRFABMS calcd for $C_8H_{15}INO_2$ (M^+ + H) 284.0148, found 284.0160. Minor isomer: colorless oil. IR ($CHCl_3$) ν 1558, 1377, 1220 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 1.30−1.33 (1H, m), 1.41−1.49 (1H, m), 1.60−1.67 (2H, m), 1.79−1.83 (4H, m), 2.00−2.31 (1H, m), 2.10−2.20 (2H, m), 2.21−2.29 (1H, m), 4.89 (1H, ddd, J = 13.2, 6.6, 2.7 Hz), 5.04 (1H, ddd, J = 10.2, 8.2, 2.1 Hz); ^{13}C NMR (150 MHz, $CDCl_3$) δ 24.9, 25.0, 26.7, 27.5, 30.8, 32.7, 32.8, 96.6; HRFABMS calcd for $C_8H_{15}INO_2$ (M^+ + H) 284.0148, found 284.0141.

4-Nitro-1-phenylbut-2-ene (14). 72% yield (as an inseparable mixture of two isomers, 91:9). Colorless oil. IR ($CHCl_3$) ν 3031, 1557, 1375, 1217 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, including the partial peaks of minor isomer) δ 3.46 (2H, d, J = 6.4 Hz), 3.50 (2H, d, J = 7.8 Hz, for minor isomer), 4.90 (2H, d, J = 7.3 Hz), 5.10 (2H, d, J = 7.8 Hz, for minor isomer), 5.81 (1H, dt, J = 15.6, 7.3 Hz), 5.88−5.91 (1H, m, for minor isomer), 6.07 (1H, dt, J = 15.6, 6.4 Hz), 7.17 (2H, d, J = 6.9 Hz), 7.23 (1H, t, J = 5.8 Hz), 7.32 (2H, t, J = 7.3 Hz); ^{13}C NMR (150 MHz, $CDCl_3$, for major isomer) δ 38.6, 77.3, 119.7, 126.5, 128.59, 128.64, 138.4, 140.0; HRFABMS calcd for $C_{10}H_{12}NO_2$ (M^++H) 178.0868, found 178.0869.

Typical Procedure for One-Pot Synthesis of Nitroalkenes. To a solution of **3a** (74.1 mg, 0.528 mmol) and $FeCl_3$ (256 mg, 0.792 mmol) in CH_3CN (2.6 mL) was added $Fe(NO_3)_3 \cdot 9H_2O$ (128 mg, 0.634 mmol), and the mixture was heated at reflux for 1 h. $LiOH \cdot H_2O$ (222 mg, 5.28 mmol) was added, and the mixture was heated at reflux for 30 min. After cooling to room temperature, the resulting suspension was diluted with Et_2O and filtered. After removal of solvent under reduced pressure, the residue was purified by chromatography (hexane/EtOAc, 10:1) to give **4a′** (80.1 mg, 82%) as a colorless oil.

(*E*)-1-Nitrodecene (4a′).[3h] 82% yield. Colorless oil. IR ($CHCl_3$) ν 2930, 1526, 1354 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.88 (3H, t, J = 6.9 Hz), 1.26−1.37 (10H, m), 1.51 (2H, dt, J = 15.1, 7.6 Hz), 2.27 (2H, q, J = 7.3 Hz), 6.98 (1H, dd, J = 13.3, 1.4 Hz), 7.28 (1H, dt, J = 13.3, 7.3 Hz); ^{13}C NMR (150 MHz, $CDCl_3$) δ 14.1, 22.6, 27.7, 28.4, 29.06, 29.08, 29.2, 31.7, 139.5, 142.9; HRFABMS calcd for $C_{10}H_{20}NO_2$ (M^+ + H) 186.1494, found 186.1501.

(*E*)-1-Nitro-2-phenylethene (4d′).[25] 66% yield. White solids, mp 51.5−52.0 °C (hexane/EtOAc, lit. 58−59 °C). IR ($CHCl_3$) ν 3020, 1635, 1525, 1346, 1259 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.43−7.57 (6H, m), 7.59 (1H, d, J = 13.7 Hz), 8.01 (1H, d, J = 13.7 Hz); ^{13}C NMR (150 MHz, $CDCl_3$) δ 129.1, 129.4, 130.0, 132.1, 137.1, 139.1 HRFABMS calcd for $C_8H_8NO_2$ (M^+ + H) 150.0555, found 150.0555.

(*E*)-1-Nitorocyclooctene (6d′).[10a] 62% yield. Colorless oil. IR ($CHCl_3$) ν 2934, 1518, 1383, 1223 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.52 (4H, br), 1.72 (4H, br), 2.30−2.36 (2H, m), 2.75 (2H, br), 7.31 (1H, t, J = 9.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 24.8, 25.6, 26.4, 26.6, 28.3, 29.0, 136.3, 152.3; HRFABMS calcd for $C_8H_{14}NO_2$ (M^+ + H)156.1025, found 156.1024.

(*E*)-1-Nitorocyclododecene (6e′).[31] 56% yield. Colorless oil. IR ($CHCl_3$) ν 2935, 1520, 1336, 1218 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 1.21−1.48 (12H, m), 1.61−1.67 (4H, m), 2.27 (2H, dd, J = 15.8, 7.6 Hz), 2.66 (2H, t, J = 6.6 Hz), 7.10 (1H, t, J = 8.6 Hz); ^{13}C NMR (150 MHz, $CDCl_3$) δ 21.9, 22.7, 23.2, 23.4, 24.6, 24.7, 24.9, 25.4, 25.7, 136.9, 152.0; HRFABMS calcd for $C_{12}H_{22}NO_2$ (M^+ + H) 212.1651, found 212.1655.

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Supporting Information Available: ^1H and ^{13}C NMR spectra for all isolated products. This material is available free of charge via the Internet at http://pubs.acs.org.

Note Added after ASAP Publication. Several errors in the Results and Discussion sections, Tables 2 and 5, and the caption of Scheme 6 appeared in the versions that was published on 11/10/2010. These were fixed when the paper was republished to the Web on 11/29/2010.

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