A Convenient Method for the Preparation of Nitro Olefins by Nitration of Olefins with Nitrogen Monoxide

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Olefins with a terminal double bond or conjugated with aromatic nucleus are successfully nitrated into nitro olefins in good-to-high yields on treatment with nitrogen monoxide (NO) in 1,2-dichloroethane. Nitro alcohols formed as by-products are dehydrated to yield nitro olefins by the subsequent treatment with acidic activated alumina. By GC analysis, it was confirmed that an equimolar amount of nitrogen gas was evolved during the present nitration. A possible reaction pathway including the formation of nitro nitroso compounds, key intermediates, is described. The key intermediates are transformed into nitro olefins by reaction with nitrogen monoxide.

Introduction of nitrogen-functions into organic compounds is one of important subjects in synthetic organic chemistry, and much effort has been made to develop practical methods of nitrogenation by using the following various reagents. For example, amines or azide are employed in nucleophilic substitution reaction of halo or hydroxy groups activated with acyl or sulfonyl groups,[1] in Michael addition to α,β-unsaturated carbonyl compounds,[2] and in ring-opening reaction of epoxides.[3,4] Several other methods are reported to introduce nitrogen-functions into olefins by using chloramine T or amines such as dimethylamine, aniline and ammonia as nitrogenating reagents in the presence of transition metals.[5]

Nitrogen monoxide (NO),[6] which is commercially available and largely produced in industries for manufacturing nitric acid, is also expected as a convenient nitrogenating reagent. Much attention has recently been paid to the chemistry of gaseous molecules in the field of biochemistry, medical science, and environmental science. Nitrogen monoxide is produced in vivo through the enzymatic reaction from guanidino group of L-arginine by nitric oxide synthase (NOS) and plays an important role as a mediator in the circulatory, immune, and nervous systems of the human body.[7] In terms of these functions, several attempts for medical treatment are now under investigation.[8] Since nitrogen monoxide is closely related to air pollution, much study has been made to develop an efficient reduction system for transformation of nitrogen monoxide into harmless reduced species such as nitrogen (N_2) or dinitrogen monoxide (N_2O).[9]

In the field of synthetic organic chemistry, however, only several reactions involving nitrogen monoxide were exemplified as practical reactions for the synthesis of nitrogen-containing compounds since nitrogen monoxide, a reactive free radical, occasionally caused unexpected formation of numerous products as shown in communications.[10,11] It was reported that olefins reacted with cobalt nitrosyl dimer in the coexistence of nitrogen monoxide to form 1,2-dinitroso alkane complex, which afforded diamines by subsequent reduction.[12] Oximes were prepared from olefins by using nitrogen monoxide and sodium borohydride in the presence of cobalt complex as a catalyst.[13] Recently, nitration of aromatic nucleus with nitrogen monoxide in the coexistence of oxygen was demonstrated.[14,15] Further, it was reported from our laboratory that the reaction of nitrogen monoxide with α,β-unsaturated carboxamides was catalyzed by cobalt(II) complex with combined use of silyl hydride to give α-nitroso carboxamides in good yields.[16] Through our continuous study on nitrogen monoxide as a nitrogenating reagent, it was found that the reaction of olefins with nitrogen monoxide proceeded in 1,2-dichloroethane to yield nitro olefins in high yields under mild conditions.[17] The nitro olefins thus produced are known as versatile synthetic intermediates[18] which undergo conjugate addition reaction, Diels–Alder reaction, [4+2] cycloaddition with vinyl ethers, and transformation into a wide variety of functional groups such as amines, oximes, and ketones.[19]

Herein, we would like to describe in detail on the simple and convenient method for the preparation of nitro olefins from olefins and nitrogen monoxide including the possible reaction pathway.

Results and Discussion

Nitration of Olefins with Nitrogen Monoxide in Various Solvents. The effect of various solvents was examined in nitration of 4-phenyl-1-butene (**1**) as a model reaction under an atmospheric pressure of nitrogen monoxide at room temperature. As shown in Table 1, haloalkanes and aromatic hydrocarbons were found to be suitable solvents for the formation of nitro olefin directly from olefin (Entries 1—5).

When 1,2-dichloroethane was employed as a solvent, the reaction started within a few minutes with the slight evolution of heat and the change in color,[20] and nitro olefin **2** was formed in 76% yield accompanied by 23% yield of nitro alcohols **3** (Entry 1). It is noted that nitration of olefin proceeded exclusively at the terminal position to give the nitro olefin and/or the nitro alcohol while yields and selectivities of nitro olefins were low in other solvents such as ethyl acetate, 1,4-dioxane, tetrahydrofuran, acetone, or acetic acid (Entries 6—10).[21] No reaction took place in tetrahydrofuran or acetone under the present mild reaction conditions, and no change in color was observed (Entries 8 and 9). Therefore, it is noted that haloalkanes and aromatic hydrocarbons are effective in forming reactive species of the present reaction.

Effect of Nitrogen Monoxide Pressure. In order to examine the effect of nitrogen monoxide pressure, nitration of olefin **1** was tried under various pressure of nitrogen monoxide. Olefin was consumed faster in accordance with the increase of nitrogen monoxide pressure. As shown in Table 2, nitrations under pressures both higher and lower than an atmospheric one caused undesirable side-reactions to result in the lowering of yields and selectivities of nitro olefins.

Dehydration of Nitro Alcohol into Nitro Olefin. As mentioned above, nitro alcohols were yielded as by-products along with the major products, nitro olefins, in the present nitration reaction. Total yield of these two nitrated products was almost quantitative, then transformation of nitro alcohols involved in the above reaction mixture into nitro olefins was tried. Various solid catalysts were examined taking dehydration of nitro alcohol **3** as a model reaction. As shown in Table 3, acidic activated alumina behaved as an efficient dehydrating reagent to afford nitro olefin in 98% yield (Entry 1) whereas neutral and basic ones[22] were not suitable.

Next, acidic activated alumina was applied to the above reaction mixture (nitro olefin 76% and nitro alcohol 23%) resulted from nitration of olefin **1**. Gentle refluxing in the presence of acidic activated alumina afforded nitro olefin **2** in 90% isolated yield (Scheme 1).

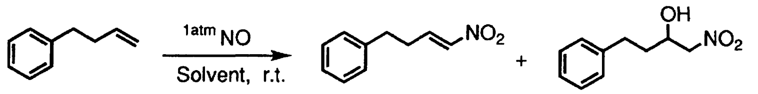
Filtration of the reaction mixture through Celite pad and evaporation of the solvent afforded nitro olefin with

Table 2. Nitration of 4-Phenyl-1-butene with Nitrogen Monoxide under Various Pressure[a)]

Entry	Pressure of NO/atm	Reaction time/h	Conversion %[b)]	Yield/%[b)] **2**	Yield/%[b)] **3**
1	0.3	20	99	58	15
2	0.5	4	98	56	20
3	1	3	100	76	23
4	2	1	99	44	22
5	5	1	100	45	24

a) Reaction conditions; 4-phenyl-1-butene 1.0 mmol, 1,2-dichloroethane 5.0 cm^3, r.t.. b) Determined by GC analysis.

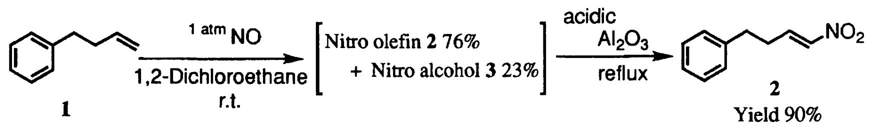
Table 1. Nitration of 4-Phenyl-1-butene with Nitrogen Monoxide in Various Solvents[a)]



1 **2** **3**

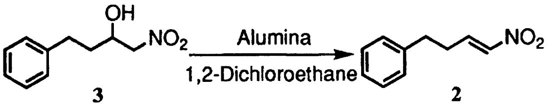
Entry	Solvent	Reaction time/h	Conversion/%[b)]	Yield/%[b)] **2**	Yield/%[b)] **3**
1	$ClCH_2CH_2Cl$	3	100	76	23
2	$BrCH_2CH_2Br$	3.5	100	76	18
3	CCl_4	1.5	94	53	25
4	PhH	1.5	95	61	23
5	PhMe	4	100	68	23
6	EtOAc	24	14	2	0
7	1,4-Dioxane	24	40	20	4
8	THF	24	0	—	—
9	Me_2CO	24	0	—	—
10	AcOH	24	100	46	15

a) Reaction conditions; 4-phenyl-1-butene 1.0 mmol, solvent 5.0 cm^3, r.t., 1 atm NO. b) Determined by GC analysis.



Scheme 1.

Table 3. Dehydration of 1-Nitro-4-phenyl-2-butanol Using Various Alumina[a)]



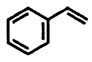
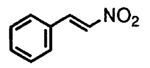
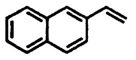
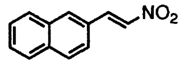
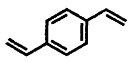
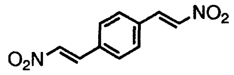
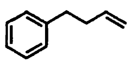
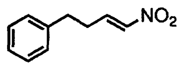
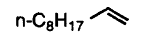
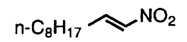
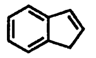
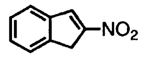
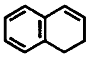
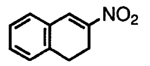
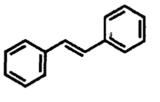
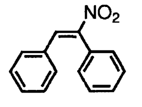
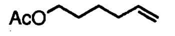
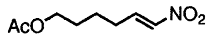
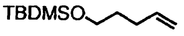
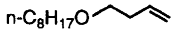
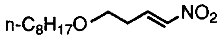
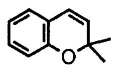
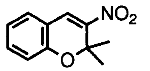
Entry	Alumina	Reaction temp °C	Conversion[b)] %	Yield[b)] %
1	Acidic	60	100	98
2	Acidic	R.T.	70	60
3	Basic	R.T.	100	15
4	Neutral	R.T.	100	17

a) Reaction conditions; 1-nitro-4-phenyl-2-butanol 0.2 mmol, 1,2-dichloroethane 5.0 cm^3. b) Determined by GC analysis.

satisfactory NMR spectrum.

Nitration of Various Olefins with Nitrogen Monoxide. The present procedure was successfully applied to various olefins. In the case of styrene and 2-vinylnaphthalene, nitro olefins **6** and **8** were obtained in 95 and 90% yields, respectively (Entries 1 and 2 in Table 4). Nitration of 1,4-divinylbenzene proceeded at two terminal positions in 88% yield (Entry 3). Olefins other than styrene derivatives were also transformed into nitro olefins in high yields (Entries 4 and 5). It should be noted that nitro group was regioselectively introduced into olefins. The present procedure was also applied to cyclic olefins conjugated with aromatic nucleus such as indene and 1,2-dihydronaphthalene, and nitro olefins having nitro group exclusively at β-position were obtained in 91 and 86% yields, respectively (Entries 6 and 7).[23)] *E*-Nitro olefin **18** was exclusively obtained irrespective of geometry of starting olefin with *cis*- (*cis*-stilbene) or *trans*- (*trans*-stilbene) configurations (Entries 8 and 9). This observation would suggest that the present nitration included the formation of alkyl radical as an intermediate which would readily

Table 4. Nitration of Various Olefins with Nitrogen Monoxide[a)]

Entry	Olefin		Nitro olefin[b)]		Yield/%[c)]
1		**5**		**6**	95
2		**7**		**8**	90
3		**9**		**10**	88
4		**1**		**2**	90
5		**11**		**12**	92
6		**13**		**14**	91
7		**15**		**16**	86[d)]
8		**17a(trans)**		**18**	85[d)]
9		**17b(cis)**			88[d)]
10		**19**		**20**	91
11		**21**		**22**	84
12		**23**		**24**	70[d)]
13		**25**		**26**	68[d)]

a) Reaction conditions; substrate 1.0 mmol, 1,2-dichloroethane 5.0 cm^3, r.t., 1 atm NO, acidic Al_2O_3 1.20 g, reflux. b) Satisfactory NMR and IR were obtained after filtration through Celite pad. c) Isolated yield. d) Purified by column chromatography on silica gel.

rotate around the carbon–carbon bond to form thermodynamically stable nitro olefin. Also olefins having acetoxy group and *t*-butyldimethylsiloxy group were converted into nitro olefins without decomposition of these functional groups (Entries 10 and 11). Nitration of 3-butenyl octyl ether and 2,2-dimethyl-2*H*-chromene afforded nitro olefins **24** and **26**, respectively, after purification by column chromatography (Entries 12 and 13).

Generation of Nitrogen Gas (N_2) in the Nitration Reaction. Introducing nitro group (NO_2) into olefins using nitrogen monoxide (NO) means that oxidation–reduction processes take place during the nitration reaction and nitrogen (N_2) or dinitrogen monoxide (N_2O)[9,24] is expected to be formed at the same time. By GC analysis, only nitrogen was detected in the nitration of 4-phenyl-1-butene (**1**) while dinitrogen monoxide was not. The quantitative analysis in accordance with reaction time revealed that nitrogen was evolved as the olefin was transformed into nitro olefin and nitro alcohol as shown in Fig. 1.

Generation of nitrogen stopped when the olefin was completely consumed after 3 h, and the amount of nitrogen was 1 to 1.4 molar amounts to that of consumed olefin. Therefore, it is reasonable to assume that nitrogen monoxide behaves not only as a source of nitrogen but also as an oxygenating reagent.

Formation of Nitrous Acid (HNO_2) in the Nitration Reaction. After the reaction completed, the solution of the reaction mixture became weakly acidic probably due to the formation of nitrous acid (HNO_2) and/or nitric acid (HNO_3). Then, quantitative analysis of nitrous acid was carried out by spectrophotometry using brucine as a color-producing reagent. After the acidic product in the reaction mixture was extracted with aqueous alkaline solution, the resulted nitrite in the aqueous layer was clearly analyzed from nitrate according to the reported procedure.[25] Actually, 0.7 molar amount of nitrite corresponding to the consumed olefin was detected. Since nitrous acid which was known to be an unstable species[26] was expected to be transformed into nitric acid as a secondary product, quantitative analysis of nitrate was also performed under different analytical conditions.[25] The spectral analysis indicated that 0.3 molar amount of nitrate existed in the aqueous solution. Consequently, the total amount of nitrite (NO_2^-) and nitrate (NO_3^-) was equimolar amount to the consumed olefin. On the basis of these results, it is suggested that one molar amount of nitrous acid (HNO_2) would probably be formed during the present nitration process. Therefore, it is reasonable to assume that nitrous acid was derived from nitrogen monoxide and terminal hydrogen in the starting olefin.

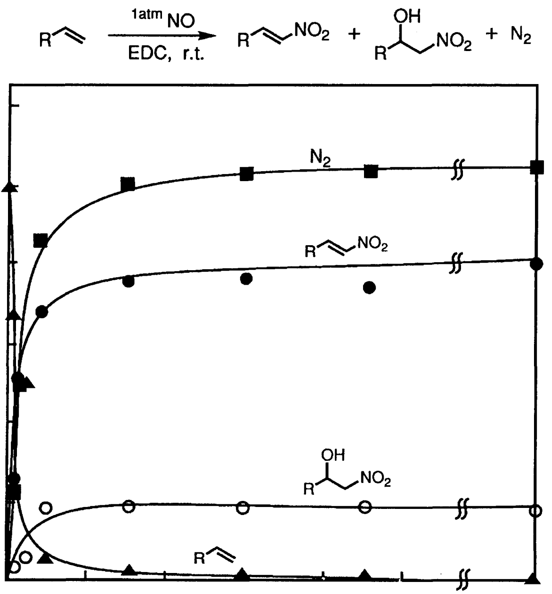


Fig. 1. The time-cource of the N_2 generation and the formation of nitrated products in the present nitration reaction (R=–$(CH_2)_2Ph$).

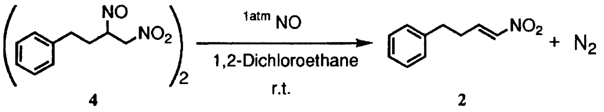
Scheme 2.

Next, nitration of olefin **1** was carried out by varying the amount of nitrogen monoxide under atmospheric pressure. When one to three molar amounts of nitrogen monoxide to the olefin was employed, unreacted olefin remained even after prolonged reaction time. While the olefin was completely consumed on treatment with four molar amounts of nitrogen monoxide. Therefore it is assumed that at least four molar amounts of nitrogen monoxide are required in the present reaction.

According to these observations, the probable stoichiometry of the formation of nitro olefins in the present reaction would be described as shown in Scheme 2.

Isolation of Nitro Nitroso Compound. As mentioned above, the participation of radical intermediate in the present reaction would cause the geometrical conversion which was observed in nitration of stilbene (Entry 8 in Table 4). It is suggested that addition-elimination reaction would proceed during the course of transformation of olefins into nitro olefins. Then, trapping of the reaction intermediates using a small amount of nitrogen monoxide was tried. Nitration of 4-phenyl-1-butene (**1**) was carried out using equimolar amount of nitrogen monoxide under atmospheric pressure. Removal of the solvent, followed by the addition of diethyl ether gave the precipitate as a white powder. This white precipitate was confirmed to be nitro nitroso compound **4** which was known to exist as a dimer[11] by NMR spectrum, infrared spectrum, and elemental analysis.

Treatment of nitro nitroso compound **4** with nitrogen monoxide under atmospheric pressure in 1,2-dichloroethane solvent at room temperature afforded nitro olefin in 57% yield (95% selectivity). By GC analysis, the amount of nitrogen evolved in the reaction would



Scheme 3.

be almost equimolar amount to the consumed nitro nitroso compound **4** as well as the conversion of olefin (Scheme 3). It was reported that the action of nitrogen monoxide on the nitroso group generated nitrogen, and diazonium nitrate was proposed as an intermediate.[27] Therefore, it would be possible to assume that diazonium nitrate was formed in the above tranformation of the nitro nitroso compound into the nitro olefin to evolve nitrogen.

Based on these results, the nitro nitroso monomer, which may exist in equilibrium with the dimer, would be formed as an intermediate in the nitration of olefin into nitro olefin, and nitrogen would be evolved during the process of transforming nitro nitroso compounds into nitro olefins (Scheme 4).

Conclusion

It is concluded that various olefins are smoothly nitrated with atmospheric pressure of nitrogen monoxide in 1,2-dichloroethane solvent at room temperature to give nitro olefins. Subsequent treatment of the resulted reaction mixture with acidic activated alumina affords nitro olefins in good-to-high yields. It is suggested that nitrogen monoxide behaves not only as a nitrogen source but also as an oxygen source of nitro group introduced into the olefin accompanied with the generation of nitrogen (N_2). The present procedure thus provides a simple and convenient method for the preparation of a variety of nitro olefins directly from olefins with a terminal double bond or conjugated with aromatic nucleus.

Experimental

General: Melting points were measured on a Mettler FP62 apparatus and uncorrected.

(a) Spectrometers: Infrared spectra were obtained by using a JASCO Model IR-700 spectrometer on KBr pellets or liquid film on KBr. Determination of the amount of nitrite and nitrate was performed by using a Shimadzu UV-160A UV-visible spectrophotometer. ^{1}H NMR spectra were recorded with a JEOL Model FX270 spectrometer using $CDCl_3$ as a solvent and with tetramethylsilane as an internal standard.

(b) Chromatography: The products were purified by preparative column chromatography on silica gel (Daiso gel IR-60). Preparative TLC was carried out on silica gel (Merck 13895, silica gel 60 F_{254}). GC analysis for organic compounds was performed on a Shimadzu GC-15A chromatograph equipped with hydrogen flame ionization detector (FID) using a glass capillary column (Shimadzu CBP-1, 25 m). For gaseous species, GC analysis was practiced on a Shimadzu GC-15A equipped with thermal conductivity detector (TCD) using a column packed with Porapack Type Q (2 m) maintained at −78 °C of column temperature by cooling the column in dry ice–methanol bath. Dinitrogen monoxide was also detected by using the same column maintained at 25 °C of column temperature. The peak areas were recorded with a Shimadzu chromatopack CR-5A.

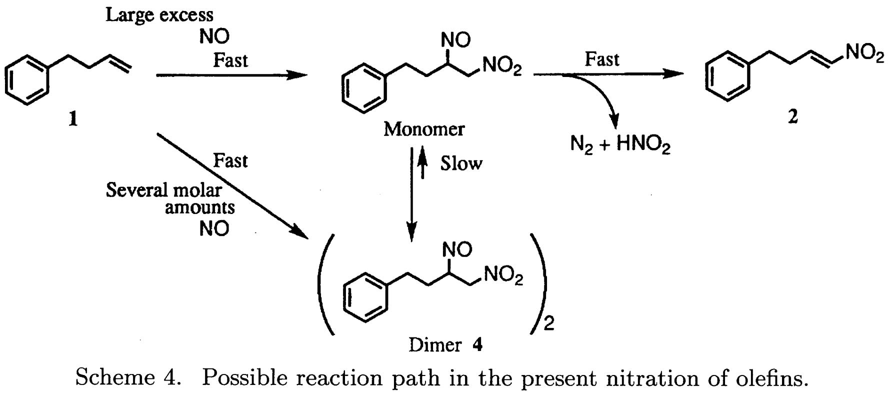
(C) Nitrogen Monoxide: Nitrogen monoxide was purchased from Nippon Sanso Corp. (purity>99%).

(d) Acidic Activated Alumina: Acidic activated alumina was purchased from E. Merck (Art. 1078, aluminum oxide 90, activity I according to Brockmann, 70—230 mesh, acidic for column chromatography).

Nitration of Olefins (Entry 1 in Table 1). The flask containing a solution of 4-phenyl-1-butene (132 mg, 1.0 mmol) in 1,2-dichloroethane (5 cm^3) was evacuated, then was filled with nitrogen monoxide gas, and the solution was stirred under an atmospheric pressure of nitrogen monoxide at room temperature for 3 h. The yields of nitro olefin and nitro alcohol were determined by GC analysis using biphenyl as an internal standard to be 76 and 23%, respectively.

Dehydration of Nitro Alcohol (Entry 1 in Table 3). A mixture of nitro alcohol **3** (39 mg, 0.20 mmol) and acidic activated alumina (100 mg) in 1,2-dichloroethane (5 cm^3) was stirred at 60 °C for 40 min. The yield of nitro olefin was determined to be 98% by GC analysis.

General Procedure for Transformation of Olefins into Nitro Olefins (Entry 4 in Table 4). The flask containing a solution of 4-phenyl-1-butene (132 mg, 1.0 mmol) in 1,2-dichloroethane (5 cm^3) was evacuated, then was filled with nitrogen monoxide gas, and the solution was stirred under an atmospheric pressure of nitrogen monoxide at room temperature. After nitrogen monoxide was released, acidic activated alumina (1.2 g) was added to the reaction mixture. The slurry was stirred under gentle reflux for 30 min. Then the reaction mixture was filtered through Celite pad



Scheme 4. Possible reaction path in the present nitration of olefins.

and the residual alumina was washed several times with 1,2-dichloroethane. Solvent was removed in vacuo to afford 1-nitro-4-phenyl-1-butene (159 mg, 90% yield based on olefin), identified by ^{1}H NMR and IR analysis.

Determination of the Amount of Nitrogen (N_2) Generated in the Present Nitration Reaction of Olefins (Fig. 1). The flask containing a solution of 4-phenyl-1-butene (132 mg, 1.0 mmol) in 1,2-dichloroethane (5 cm^3) was evacuated, then was filled with nitrogen monoxide gas, and the solution was stirred under an atmospheric pressure of nitrogen monoxide at room temperature. After prescribed reaction time, the gas phase in the reaction system was quantitatively analyzed by gas chromatography.

Determination of the Amount of Nitrous Acid (HNO_2) Formed in the Present Nitration Reaction of Olefins. To the solution of the reaction mixture, 1 mol dm^{-3} aqueous sodium hydroxide (12 cm^3) was added, and the acidic products was extracted with distilled water several times. The combined aqueous layer was made up to 100 cm^3 with distilled water, and then 1 cm^3 of the aqueous solution was further diluted to 100 cm^3. The concentrated organic layer was also diluted with distilled water in the same manner. The amount of nitrite and nitrate in these diluted solutions was determined by spectrophotometry according to the reported method.[25)]

Isolation of 1-Nitro-2-nitroso-4-phenylbutane (4) (Scheme 3). The flask containing a solution of 4-phenyl-1-butene (396 mg, 3.0 mmol) in 1,2-dichloroethane (15 cm^3) was evacuated, then was filled with nitrogen monoxide gas (73 cm^3), and the solution was stirred under an atmospheric pressure of nitrogen monoxide at room temperature. After nitrogen monoxide was released, solvent was removed in vacuo. To the concentrated reaction mixture was added diethyl ether to form white precipitate. The precipitate was collected by filtration, washed with diethyl ether, and dried in vacuo to afford nitro nitroso compound **4** as a white powder (58 mg). ^{1}H NMR ($CDCl_3$) δ=7.25 (5H, m), 6.11—6.00 (1H, m), 5.15 (1H, dd, J=10.4 and 15.3 Hz), 4.50 (1H, dd, J=3.05 and 15.3 Hz), 2.70 (2H, t, J=7.33 Hz), 2.30—2.00 (2H, m); ^{13}C NMR ($CDCl_3$) δ=139.3, 128.9, 128.4, 126.8, 72.9, 63.7, 31.2, 30.2; IR (KBr) 1555, 1399, 1377, 1228 cm^{-1}. Found: C, 57.9; H, 5.8; N, 13.6%. Calcd for $C_{10}H_{12}N_2O_3$: C, 57.7; H, 5.8; N, 13.5%.

Reaction of Nitro Nitroso Compound with Nitrogen Monoxide (Scheme 3). A slurry of nitro nitroso compound **4** (104 mg, 0.50 mmol as a monomer) in 1,2-dichloroethane (5 cm^3) was stirred under atmospheric pressure of nitrogen monoxide at room temperature for 24 h. After nitrogen monoxide was released, yield and conversion were determined by GC and/or ^{1}H NMR.

^{1}H NMR and IR Spectra of Nitro Olefins (Table 4). β-Nitrostyrene (6): Mp 56—57 °C (lit,[28)] 56—58 °C); ^{1}H NMR ($CDCl_3$) δ=8.01 (1H, d, J=14.0 Hz), 7.62—7.45 (6H, m); IR (KBr) 1636, 1519, 1344 cm^{-1}.

1-(2-Naphthyl)-2-nitroethylene (8): Mp 120—122 °C (lit,[29)] 120.5—122 °C); ^{1}H NMR ($CDCl_3$) δ=8.15 (1H, d, J=13.4 Hz), 8.02 (1H, s), 7.95—7.85 (3H, m), 7.70 (1H, d, J=13.4 Hz), 7.65—7.53 (3H, m); IR (KBr) 1631, 1508, 1332 cm^{-1}.

1,4-Bis(2-nitrovinyl)benzene (10): Mp 216—221 °C (decomp); ^{1}H NMR ($CDCl_3$) δ=8.00 (2H, d, J=13.4 Hz), 7.64 (4H, s), 7.63 (2H, d, J=13.4 Hz); IR (KBr) 1632, 1500, 1331 cm^{-1}; HRMS Found: m/z 220.0503. Calcd for $C_{10}H_8O_4N_2$: M, 220.0484.

1-Nitro-4-phenyl-1-butene (2): Bp 235 °C/0.7 mmHg (Kugel rohr bath temp) (1 mmHg=133.322 Pa); ^{1}H NMR ($CDCl_3$) δ=7.34—7.15 (6H, m), 6.95 (1H, d, J=13.4 Hz), 2.83 (2H, t, J=7.3 Hz), 2.63—2.54 (2H, m); IR (KBr) 1648, 1524, 1351 cm^{-1}; HRMS Found: m/z 177.0809. Calcd for $C_{10}H_{11}NO_2$: M, 177.0790.

1-Nitro-1-decene (12): ^{1}H NMR ($CDCl_3$) δ= 7.33—7.22 (1H, m), 6.98 (1H, d, J=13.5 Hz), 2.31—2.22 (2H, m), 1.58—1.49 (2H, m), 1.28 (10H, br), 0.89 (3H, t, J=7.3 Hz); IR (KBr) 1647, 1526, 1352 cm^{-1}.

2-Nitroindene (14): Mp 139—140 °C (lit,[30)] 139—140 °C); ^{1}H NMR ($CDCl_3$) δ=7.92 (1H, s), 7.54—7.32 (4H, m), 3.99 (2H, s); IR (KBr) 1653, 1499, 1336 cm^{-1}.

3-Nitro-1,2-dihydronaphthalene (16): ^{1}H NMR ($CDCl_3$) δ=7.84 (1H, s), 7.38—7.18 (4H, m), 3.01 (4H, s); IR (KBr) 1645, 1506, 1326 cm^{-1}; HRMS Found: m/z 175.0633. Calcd for $C_{10}H_9NO_2$: M, 175.0634.

(*E*)-α-Nitrostilbene (18): Mp 74 °C; ^{1}H NMR ($CDCl_3$) δ=8.23 (1H, s), 7.52—7.07 (10H, m); IR (KBr) 1650, 1519, 1323 cm^{-1}.

6-Nitro-5-hexenyl Acetate (20): Bp 250—255 °C/0.01 mmHg (Kugel rohr bath temp); ^{1}H NMR ($CDCl_3$) δ=7.32—7.22 (1H, m), 7.00 (1H, d, J=13.4 Hz), 4.09 (2H, t, J=6.1 Hz), 2.37—2.31 (2H, m), 2.06 (3H, s), 1.76—1.55 (4H, m); IR (neat) 1738, 1649, 1525, 1353 cm^{-1}; HRMS Found: m/z 188.0931. Calcd for $C_8H_{14}NO_4$: (M+H), 188.0923.

5-(*t*-Butyldimethylsiloxy)-1-nitro-1-pentene (22): Bp 220—225 °C/0.3 mmHg (Kugel rohr bath temp); ^{1}H NMR ($CDCl_3$) δ=7.37—7.27 (1H, m), 7.00 (1H, d, J=13.4 Hz), 3.66 (2H, t, J=5.5 Hz), 2.41—2.33 (2H, m), 1.77—1.67 (2H, m), 0.89 (9H, s), 0.05 (6H, s); IR (neat) 1649, 1527, 1352 cm^{-1}; HRMS Found: m/z 246.1519. Calcd for $C_{11}H_{24}NO_3Si$: (M+H), 246.1525.

4-Nitro-3-butenyl Octyl Ether (24): ^{1}H NMR ($CDCl_3$) δ=7.36—7.26 (1H, m), 7.06 (1H, d, J=13.4 Hz), 3.57 (2H, t, J=6.1 Hz), 3.42 (2H, t, J=6.7 Hz), 2.56—2.49 (2H, m), 1.28 (10H, br), 0.88 (3H, t, J=6.7 Hz); IR (neat) 1649, 1528, 1353 cm^{-1}; HRMS Found: m/z 230.1763. Calcd for $C_{12}H_{24}NO_3$: (M+H), 230.1756.

2,2-Dimethyl-3-nitro-2*H*-chromene (26): ^{1}H NMR ($CDCl_3$) δ=7.63 (1H, s), 7.36—7.20 (2H, m), 7.00—6.86 (2H, m), 1.74 (6H, s); IR (neat) 1640, 1515, 1314 cm^{-1}; HRMS Found: m/z 205.0761. Calcd for $C_{11}H_{11}NO_3$: M, 205.0739.

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$$\text{R-NO} \xrightarrow{\text{2 NO}} \text{R-N}_2\text{ONO}_2 \xrightarrow{\text{NO}} \text{R}\bullet + \text{N}_2 + 2\text{NO}_2$$

Scheme 5.

shown in Scheme 5 (Ref. 11).

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