EurJOC European Journal of Organic Chemistry

FULL PAPER

DOI: 10.1002/ejoc.201402750

Oxone®/KI-Mediated Nitration of Alkenes and Alkynes: Synthesis of Nitro- and β-Iodonitro-Substituted Alkenes

Sornsiri Hlekhlai,[a] Natthapol Samakkanad,[a] Tassaporn Sawangphon,[a] Manat Pohmakotr,[a] Vichai Reutrakul,[a] Darunee Soorukram,[a] Thaworn Jaipetch,[b] and Chutima Kuhakarn*[a]

Keywords: Synthetic methods / Green chemistry / Alkenes / Alkynes / Oxidation / Nitration

Oxone® ($2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$) was used to promote the nitration of alkenes and alkynes with sodium nitrite ($NaNO_2$) and potassium iodide (KI). This stable, easy-to-handle, and environmentally benign oxidant was used under mild conditions (room temperature) and provided short reaction times. Styrene derivatives that did not contain electron-donating groups afforded the corresponding nitro alkenes in moderate to good yields, whereas aliphatic alkenes and electron-deficient alkenes were not good substrates. Under similar reaction conditions, aryl alkynes yielded β-iodonitro alkenes.

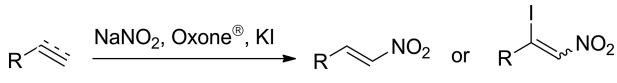
Introduction

Nitro alkenes are an important class of nitro compounds that can be synthetically useful for the preparation of a variety of organic compounds for use in various fields.[1] Nitro alkene-containing molecules have also been reported to exhibit important biological activities.[2] The nitro group has an activating effect on the adjacent carbon-carbon double bond, which enables the nitro alkene to serve as a Michael acceptor[3] and an electron-deficient dienophile partner[4] in a cycloaddition reaction. Furthermore, the nitro group can be transformed into other important functionalities, allowing the nitro group to serve as a transient activating functional group.[5] Several synthetic methods have been reported for the synthesis of nitro alkenes. Among them, the Henry reaction followed by a dehydration is a classical method for the preparation of nitro alkenes.[6] Alternatively, nitro alkenes can be prepared by the direct nitration of alkenes with MNO_2 (M = Na, K, or Ag),[7a–7j] nitrogen dioxide (NO_2),[7k] nitric oxide (NO)[7l–7n] or clay-supported nitrating reagents[7o] as well as by the decarboxylative nitration of α,β-unsaturated carboxylic acids.[8] Although these procedures have been well described, significant developments in both the nitration of alkenes and decarboxylative nitration have recently received much attention.[9] However, several drawbacks including gaseous and harsh conditions, refluxing conditions, the formation of undesired (*E*) and (*Z*) isomers, expensive reagents, and lengthy reaction times might be encountered.

The development of environmentally benign, experimentally simple, and efficient synthetic strategies continues to attract interest and is an important subject of research because of economical, environmental, and green chemistry objectives. Oxone® ($2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$) is a colorless, granular, free-flowing, solid peroxygen compound that serves as powerful non-chlorine oxidizing agent that is stable, easy-to-handle, nontoxic, and relatively inexpensive. Additionally, the byproducts associated with Oxone® are generally recognized as environmental safe. Because of its stability, high efficiency, experimentally simple procedures, mild reaction conditions, and generation of minimal chemical waste, Oxone® has found many synthetic applications.[10] Because the direct installation of a nitro moiety at an olefinic carbon is a powerful method to access nitro alkenes, we developed a convenient, practical, and environmentally benign synthetic method for the nitration of alkenes. We then chose Oxone® as a benign oxidant to mediate the nitration of alkenes and alkynes.

Results and Discussion

As a part of our ongoing interest in oxidative transformation reactions,[11] we herein report an eco-friendly reaction that uses the sodium nitrite ($NaNO_2$)/Oxone®/KI combination to effect the nitration of alkenes and alkynes (see Scheme 1).



Scheme 1. Synthesis of nitro alkenes using $NaNO_2$/Oxone®/KI.

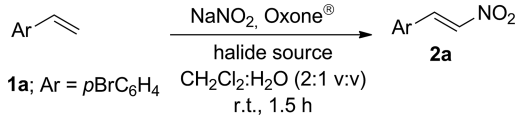
[a] Department of Chemistry and Center of Excellence for Innovation in Chemistry (PERCH-CIC), Faculty of Science, Mahidol University,
Rama VI Road, Bangkok 10400, Thailand
E-mail: chutima.kon@mahidol.ac.th
http://chemistry.sc.mahidol.ac.th
[b] Mahidol University, Kanchanaburi Campus, Saiyok, Kanchanaburi 71150, Thailand

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/ejoc.201402750.

p-Bromostyrene (**1a**) was chosen as a model substrate to examine the optimum reaction conditions (see Table 1). Initially, the treatment of a mixture of *p*-bromostyrene (**1a**, 0.5 mmol), Oxone® (1 equiv.), and KI (1.0 equiv.) in CH_2Cl_2 (2 mL) with a solution of $NaNO_2$ (3 equiv.) in H_2O (1 mL) resulted in the generation of heat and the vigorous evolution of gas. Monitoring by TLC analysis revealed that **1a** still remained, and the desired nitro alkene **2a** was isolated in 15% yield (see Table 1, Entry 1). Thus, we treated the reaction mixture with $NaNO_2$ in a portionwise manner. A suspended mixture of **1a** (0.5 mmol), Oxone® (1 equiv.), and KI (1.0 equiv.) in CH_2Cl_2 (2 mL) was treated with a solution of $NaNO_2$ (1 equiv.) in water (1 mL) at room temperature. After the reaction was stirred for 15 min, additional solid $NaNO_2$ (4 equiv., 1 equiv. every 15 min) was introduced to the reaction vessel. After the last portion of solid $NaNO_2$ was added, the reaction mixture was stirred for an additional 0.5 h. After a routine aqueous workup, **2a** was obtained in the low yield of 29% (see Table 1, Entry 2). Employing an excess amount of Oxone® (2.4 equiv.) led to a dramatic increase in the yield to give nitro alkene **2a** in 88% isolated yield (see Table 1, Entry 3). When the reaction was carried out with a higher ratio of water to dichloromethane, a mixture of nitro alkene **2a** and β-iodonitro compound **3a** was obtained in a ratio of 7:2 (**2a**/**3a**, by integration of the ^1H NMR signals, see Table 1, Entry 4). However, the mixture slowly turned brown, and **3a** was converted into **2a** upon standing at room temperature. Inferior results were obtained when the reactions were conducted in Et_2O/H_2O and $ClCH_2CH_2Cl/H_2O$ (see Table 1, Entries 5 and 6). Increasing the stoichiometric amount of either Oxone® (from 2.4 equiv. to 4 equiv.) or KI (from 1 equiv. to 2 equiv.) led to lower yields of **2a** (see Table 1, Entries 7 and 8). Finally, a dramatic decrease in the reaction yield was observed when KI was employed in a substoichiometric amount (see Table 1, Entry 9). However, in all cases, (*E*)-nitro alkene **2a** was obtained as a single isomer.

Having established the optimum reaction conditions (see Table 1, Entry 3), the halide source was next examined. An array of halide sources were screened, which included NaI, Et_4NI, KBr, and NaCl, and the results are summarized in Table 2. The iodide anion promoted the reaction more efficiently than the bromide and chloride ions. Potassium iodide (KI) promoted the reaction most efficiently.

Table 2. Optimization of the halide sources.[a]

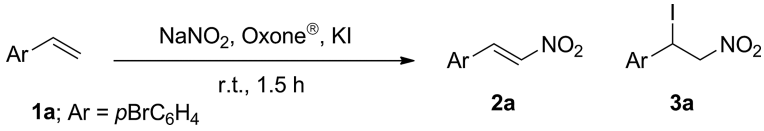


Entry	Halide source	Yield [%][b]
1	KI	88
2	NaI	78
3	Et_4NI	55
4	KBr	27
5	NaCl	trace

[a] Compound **1a** (0.5 mmol), Oxone® (2.4 equiv.), and halide source (1 equiv.) were suspended in CH_2Cl_2 (2 mL), and then a solution of $NaNO_2$ (1 equiv.) in water (1 mL) was added at room temperature. The reaction was stirred for 15 min, and then solid $NaNO_2$ (4 equiv., 1 equiv. every 15 min) was added portionwise. [b] Isolated yield.

On the basis of these results (see Tables 1 and 2), the optimized reaction conditions were further employed to explore the generality and functional group compatibility of this reaction. The nitration of styrene derivatives was primarily examined (see Table 3). Under the standard reaction conditions, some substrates gave a mixture of nitro alkene **2** and the corresponding β-iodonitro compound **3**. In these cases, the mixture was treated with aqueous NaOH (10 M, 1 mL) upon completion of the reaction (1.5 h), and the resulting mixture was heated at reflux for 1 h. Halogen-substituted styrene derivatives, which included the 4-Br, 4-Cl, 3-Cl, 2-Cl, 4-F, and 3-F substituents, as well as styrene under-

Table 1. Optimization of reaction conditions.[a]

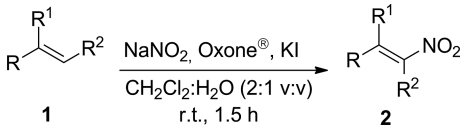


Entry	Oxone® [equiv.]	KI [equiv.]	$NaNO_2$ [equiv.]	Solvent [v/v]	**2a**/**3a**[b]	% Yield **2a**[c]
1	1	1	3[d]	CH_2Cl_2/H_2O (2:1)	–	15
2	1	1	5	CH_2Cl_2/H_2O (2:1)	–	29
3	2.4	1	5	CH_2Cl_2/H_2O (2:1)	–	88
4	2.4	1	5	CH_2Cl_2/H_2O (1:2)	7:2	–
5	2.4	1	5	Et_2O/H_2O (2:1)	–	32
6	2.4	1	5	$ClCH_2CH_2Cl/H_2O$ (2:1)	–	68
7	4	1	5	CH_2Cl_2/H_2O (2:1)	–	56
8	2.4	2	5	CH_2Cl_2/H_2O (2:1)	–	72
9	2.4	0.5	5	CH_2Cl_2/H_2O (2:1)	–	49

[a] Unless otherwise noted, **1a** (0.5 mmol), Oxone®, and KI were suspended in the organic solvent, and then a solution of $NaNO_2$ (1 equiv.) in water was added at room temperature. The reaction was stirred for 15 min, and then solid $NaNO_2$ (4 equiv., 1 equiv. every 15 min) was added portionwise. [b] After chromatographic purification, the product ratio was determined by analyzing the integration of the ^1H NMR (300 MHz) signals for the mixture. [c] Isolated yield. [d] A solution of $NaNO_2$ in water was added to the reaction vessel in one portion.

went the reaction to provide the corresponding nitro alkenes **2a**–**2g** in good yields (75–88%, see Table 3, Entries 1–7). Styrenes that contained strong electron-withdrawing groups such as $–NO_2$ and –CHO readily underwent the reaction to give the corresponding nitro alkenes **2h**–**2j** in moderate yields (53–69%, see Table 3, Entries 8–10). Both $ClCH_2$– and acetoxy (AcO–) substituents were well tolerated under the standard reaction conditions to provide **2k** and **2l** in 73 and 62% yield, respectively (see Table 3, Entries 11 and 12).

Table 3. Nitration reaction of styrene derivatives.[a]



1 **2**

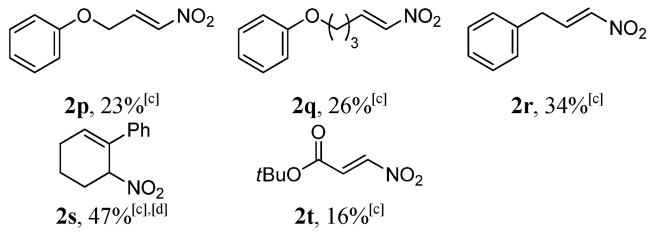
Entry	R	R^1	R^2	Product **2**	Yield [%][b]
1	4-BrC_6H_4	H	H	**2a**	88
2	4-ClC_6H_4	H	H	**2b**	80
3[c]	3-ClC_6H_4	H	H	**2c**	87
4[c]	2-ClC_6H_4	H	H	**2d**	83
5	4-FC_6H_4	H	H	**2e**	80
6[c]	3-FC_6H_4	H	H	**2f**	82
7[c]	C_6H_5	H	H	**2g**	75
8	4-$O_2NC_6H_4$	H	H	**2h**	53
9	3-$O_2NC_6H_4$	H	H	**2i**	69
10	3-$OHCC_6H_4$	H	H	**2j**	68
11[c]	4-$(ClCH_2)C_6H_4$	H	H	**2k**	73
12	4-$AcOC_6H_4$	H	H	**2l**	62
13[c]	4-*t*BuC_6H_4	H	H	**2m**	35
14[c]	C_6H_5	H	Me	**2n**	68[d]
15[c]	1-naphthyl	H	H	**2o**	42

[a] Compound **1** (0.5 mmol), Oxone® (2.4 equiv.), and KI (1 equiv.) were suspended in CH_2Cl_2 (2 mL), and then a solution of $NaNO_2$ (1 equiv.) in water (1 mL) was added at room temperature. The reaction was stirred for 15 min, and then solid $NaNO_2$ (4 equiv., 1 equiv. every 15 min) was added portionwise. [b] Isolated yield. [c] After 1.5 h, aqueous NaOH (10 M, 1 mL) was added, and the mixture was heated at reflux for 1 h. [d] Yield of (*E*) isomer only.

Unfortunately, the reaction was incompatible with styrene derivatives that contained an electron-donating substituent. The reactions of 4-methylstyrene and 4-methoxystyrene showed unidentified spots on the TLC plate, but the starting materials were completely consumed. This is probably a result of competing reactions such as a benzylic oxidation or the iodination or nitration of the aromatic ring.[11] 4-*tert*-Butylstyrene gave a low yield (35% yield) of the corresponding nitro alkene **2m** (see Table 3, Entry 13). The sterically hindered β-methylstyrene gave a mixture of (*E*) and (*Z*) isomers (*E*/*Z*, 8:1, by integration of the ^1H NMR signals) in 78% yield. The single (*E*) isomer was obtained in 68% yield after preparative thin layer chromatography (see Table 3, Entry 14). 1-Vinylnaphthalene gave the corresponding nitro alkene **2o** in 42% yield (see Table 3, Entry 15). Finally, 2-vinylpyridine and 4-vinylpyridine, both vinyl-substituted heteroaromatic compounds, were examined. Unfortunately, the desired nitro alkenes were not detected. The crude residues contained insoluble mixtures, and the starting materials were recovered.

The nitration reactions of aliphatic alkenes as well as an α,β-unsaturated ester were also investigated, and the results are summarized in Table 4. Under the reported reaction conditions, aliphatic alkenes gave poorer results than those observed with styrene derivatives, and the corresponding nitro alkenes **2p**–**2r** were afforded in low yields (23–34% yields) without isomerizing into their corresponding allylic nitro compounds. 1-Phenylcyclohexene gave 6-nitro-1-phenylcyclohexene (**2s**), an allylic nitrocyclohexene, as the product in 47% yield instead of α,β-unsaturated 1-nitro-2-phenylcyclohexene.[12] We reasoned that this exception, in the case of 1-phenylcyclohexene, resulted from the restricted conformation within the cyclohexane ring that is required for the elimination of HI. Compound **2s** was also produced when the nitration reaction of 1-phenylcyclohexene was carried out under ultrasonic conditions with $NaNO_2$/ceric ammonium nitrate (CAN)/AcOH in a sealed tube at 600 W.[7i] 6-Nitro-1-phenylcyclohexene (**2s**) was reported to be thermodynamically more stable than 1-nitro-2-phenylcyclohexene, its α,β-unsaturated isomer, because the steric interaction between the nitro and phenyl group in the latter compound hinders either group from conjugating well with the olefinic moiety.[13] In contrast to the reaction of 1-phenylcyclohexene, those of cyclohexene and norbornene did not perform well, and unidentified spots on the TLC plate and complex ^1H NMR patterns were observed. Attempts to conduct the nitration of α,β-unsaturated carbonyl compounds were also unsatisfactory. Among several substrates examined, the reaction of *tert*-butyl acrylate gave the corresponding β-nitro derivative **2t** in only 16% yield. Although the reactions of aliphatic alkenes and electron-deficient alkenes looked clean (TLC analysis indicated recovery of starting material, product, and baseline substance), they resulted in a poor mass recovery of the crude mixture (less than 40% of the theoretical yield).

Table 4. Nitration reaction of aliphatic alkenes and α,β-unsaturated ester.[a,b]



2p, 23%[c] **2q**, 26%[c] **2r**, 34%[c]

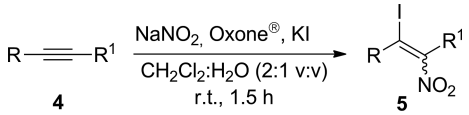
2s, 47%[c,d] **2t**, 16%[c]

[a] Compound **1** (0.5 mmol), Oxone® (2.4 equiv.), and KI (1 equiv.) were suspended in CH_2Cl_2 (2 mL), and then a solution of $NaNO_2$ (1 equiv.) in water (1 mL) was added at room temperature. The reaction was stirred for 15 min, and then solid $NaNO_2$ (4 equiv., 1 equiv. every 15 min) was added portionwise. [b] Isolated yields are provided. [c] After 1.5 h, solid $LiOH·H_2O$ (10 equiv.) was added, and the mixture was heated at reflux for 1 h. [d] 1-Phenylcyclohexene was employed as the starting material.

The synthesis of β-iodonitro alkenes has rarely been reported.[14] As an extension of the present work, it was of interest to study the nitration of alkynes, and the results are

summarized in Table 5. Under the standard reaction conditions for styrene derivatives, the reaction of phenylacetylene afforded β-iodonitro alkene **5a** in 62% yield as a mixture of (*E*) and (*Z*) isomers (see Table 5, Entry 1). Next, arylacetylenes that contained substituents with different electronic properties, such as Me–, MeO–, Br–, F–, and $–NO_2$, were evaluated (see Table 5, Entries 2–8). In all cases, the corresponding β-iodonitro alkenes **5b**–**5h** were obtained in low to moderate yields (20–70% yields) and as an inseparable mixture of (*E*) and (*Z*) isomers. In the case of 4-ethynylanisole (see Table 5, Entry 3), (*E*)-1-(1,2-diiodovinyl)-4-methoxybenzene (**6**) was obtained (30% yield) as a significant competing product. This may be attributed to the strong electron-releasing properties of the methoxy group (MeO–), which facilitated the iodination reaction. Additionally, the formation of **6** suggests that molecular iodine (I_2) was generated under the reaction conditions. This was confirmed by the isolation of **6** in quantitative yield without the formation of **5c** when 4-ethynylanisole was exposed to the standard reaction conditions, but I_2 (1 equiv.) was employed in place of KI/Oxone®. In the case of 1-phenylpropyne, the reaction proceeded smoothly to give the corresponding product **5i** as a mixture of isomers in 53% yield (see Table 5, Entry 9). On the basis of the spectroscopic data of β-iodonitro alkene **5b**, which was derived from 4-ethynyltoluene (**4b**), the major isomer was confirmed to have the (*E*) configuration in which the iodine atom was oriented anti to the nitro group (NOE experiments, see Supporting Information). The stereochemistry of compounds **5a** and **5c**–**5i** were then assigned on the basis of those of **5b**. Finally, the aliphatic alkynes 1-octyne and 4-octyne failed to provide the desired β-iodonitro alkene products. The crude reaction mixture showed an imbalance of the recovered mass, and the starting alkynes could not be recovered.

Table 5. Nitration reaction of arylacetylenes.[a]

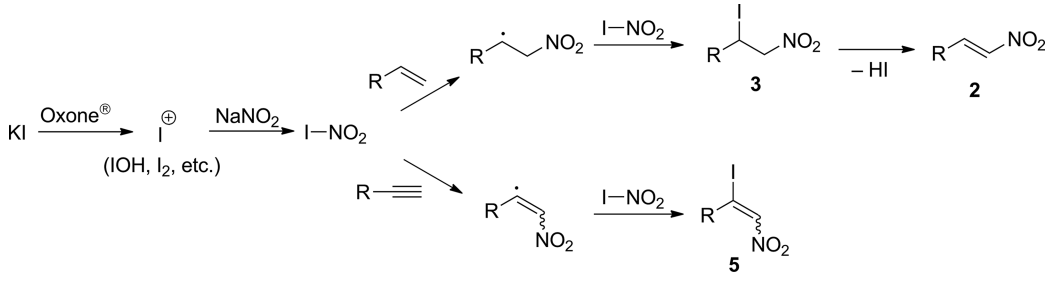


4 5

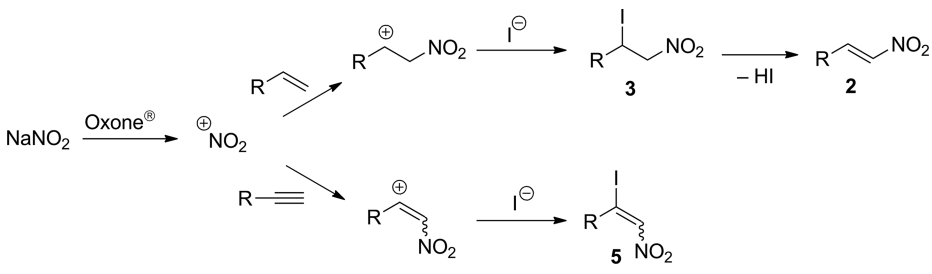
Entry	R	R^1	Product **5**	Yield [%][b]	*E*/*Z*[c]
1	C_6H_5	H	**5a**	62	5.6:1
2	4-MeC_6H_4	H	**5b**	70	4.8:1
3	4-$MeOC_6H_4$	H	**5c**	20[d]	4.2:1
4	4-BrC_6H_4	H	**5d**	63	6.7:1
5	2-BrC_6H_4	H	**5e**	57	9.1:1
6	4-FC_6H_4	H	**5f**	65	5.9:1
7	3-FC_6H_4	H	**5g**	48	6.3:1
8	4-$O_2NC_6H_4$	H	**5h**	26	3.4:1
9	C_6H_5	Me	**5i**	53	4.7:1

[a] Compound **4** (0.5 mmol), Oxone® (2.4 equiv.), and KI (1 equiv.) were suspended in CH_2Cl_2 (2 mL), and then a solution of $NaNO_2$ (1 equiv.) in water (1 mL) was added at room temperature. The reaction was stirred for 15 min, and then solid $NaNO_2$ (4 equiv., 1 equiv. every 15 min) was added portionwise. [b] Isolated yield. [c] The *E*/*Z* ratios were determined from by ^{1}H NMR analysis (300 or 400 MHz). [d] (*E*)-1-(1,2-Diiodovinyl)-4-methoxybenzene (**6**) was isolated in 30% yield.

Although no detailed mechanistic studies have been carried out, on the basis of the above experimental results, two pathways involving radical and ionic mechanisms are possibly taking place (see Schemes 2 and 3). For a radical nitration, the oxidation of KI with Oxone® takes place in the first step to generate an electrophilic iodine species (i.e., IOH or I_2).[15] Although it is probably generated under our reaction conditions, molecular iodine (I_2 in place of KI/Oxone®) was not capable of mediating the nitration reaction of styrene, and no reaction took place with the styrene unconsumed (by ^{1}H NMR analysis of the crude mixture).



Scheme 2. Proposed radical nitration of alkenes and alkynes.



Scheme 3. Proposed ionic nitration of alkenes and alkynes.

The subsequent reaction of the electrophilic iodine species with $NaNO_2$ leads to the formation of the I–NO_2 species.[7f] Thus, the nitryl radical ($^{\cdot}NO_2$), which is generated from the I–NO_2 species, preferentially undergoes a reaction at the less-hindered side of the alkene or alkyne to generate the more stable secondary or vinylic radical, respectively. The radical intermediate is then trapped by the iodine atom to lead to β-iodonitro alkane **3** or β-iodonitro alkene adduct **5**. In some cases with the formation of a β-iodonitro alkane **3**, there is the spontaneous elimination of HI. Otherwise the two-step reaction sequence in one pot requires a base-induced dehydroiodination to give the corresponding nitro alkene product **2**. In support of the radical mechanism, the nitration reaction of *p*-bromostyrene (**1a**) was carried out in the presence of the radical inhibitor TEMPO [(2,2,6,6-tetramethylpiperidin-1-yl)oxyl, 1 equiv.]. As a result, the yield of nitro alkene **2a** was drastically reduced to 34% yield, and the *p*-bromostyrene (**1a**) still remained (by TLC analysis prior to the aqueous workup). Although this observation implies that the reaction may proceed through a radical pathway, the lower yield of **2a** might result from competing reactions of TEMPO with Oxone® or other generated reactive species.[16]

Although, the radical nitration pathway can convert alkenes into nitro alkenes, the cationic nitration pathway should not be excluded. The inferior results obtained when electron-deficient-substituted styrene derivatives, aliphatic alkenes, α,β-unsaturated carbonyl compounds, and electron-deficient-substituted arylacetylenes were employed as substrates suggest the involvement of an electrophilic nitronium ion ($^{+}NO_2$), which is generated from the reaction of Oxone® and $NaNO_2$ as the reactive electrophile.[11c] Thus, the nitronium ion attacks the alkene or alkyne to lead to a secondary or vinylic cation, which is then trapped by an iodide ion to yield β-iodonitro alkane **3** or β-iodonitro alkene adduct **5**. Subsequent HI elimination or base-mediated HI elimination of β-iodonitro alkane **3** gives nitro alkene **2** as the product.

Conclusions

In summary, we have reported a convenient, mild, and rapid method for the nitration of alkenes into their corresponding nitro alkenes. Styrene derivatives that did not contain electron-donating groups yielded the corresponding nitro alkenes in moderate to good yields, whereas aliphatic and electron-deficient alkenes gave deficient results. In addition, this method can be applied to the synthesis of β-iodonitro alkenes by starting from phenylacetylenes. Despite the limited scope of substrates, in view of the convenient and mild reaction conditions (room temperature) as well as the relatively inexpensive reagents, the present approach is a significant alternative to existing methods for the synthesis of nitro alkenes and β-iodonitro alkenes, which are an important class of compounds in organic chemistry.

Experimental Section

General Methods: All reagents were obtained from commercial sources and used without further purification. Preparative and thin layer chromatography was carried out on TLC alumina sheets with silica gel 60 F_{254} (Merck). Column chromatography was performed with silica gel (Merck) and a hexanes/acetone mixture as the eluent, and all solid compounds were recrystallized from a hexanes/CH_2Cl_2 mixture. Melting points were recorded with a digital Electrothermal Melting 9100 apparatus. The ^1H and ^{13}C NMR spectroscopic data were recorded with Bruker 300 (300 MHz) and Bruker 400 (400 MHz) spectrometers, and $CDCl_3$ or [D_6]acetone was used as the solvent. The ^1H NMR chemical shifts are reported in ppm by using tetramethylsilane (TMS) as the internal standard. The ^{13}C NMR chemical shifts are reported in ppm by using the residual non-deuterated solvent peak as the internal standard. The IR spectra were recorded with a Perkin–Elmer EX FTIR spectrometer. The mass spectra were recorded with a Thermo Finnigan Polaris Q mass spectrometer. The high resolution mass spectra were recorded with an HR-TOF-MS Micromass model VQTOF2 mass spectrometer.

General Procedure A – One-Step Synthesis of Nitro Olefins and β-Iodo Nitro Alkenes: To a mixture of the alkene or alkyne (0.5 mmol), Oxone® (368.9 mg, 1.2 mmol), and KI (83.5 mg, 1.0 mmol) was added dichloromethane (2 mL). To this solution was slowly added a solution of $NaNO_2$ (34.5 mg, 0.5 mmol) in water (1 mL). The mixture was stirred at room temperature for 15 min, and then solid $NaNO_2$ (4 equiv., 1 equiv. every 15 min) was added portionwise. After the final amount of $NaNO_2$ was introduced, the mixture was stirred for an additional 15 min. The reaction was then quenched by the addition of saturated aqueous sodium thiosulfate (5 mL). The resulting mixture was further stirred and then extracted with EtOAc (3× 10 mL). The combined organic extracts were washed with water (10 mL) and brine (10 mL). The organic layer was dried with anhydrous $MgSO_4$ and concentrated under reduced pressure. The residue was purified by column chromatography (hexanes/acetone).

General Procedure B – Two-Step Synthesis of Nitro Olefins: To a mixture of the alkene (0.5 mmol), Oxone® (368.9 mg, 1.2 mmol), and KI (83.5 mg, 1.0 mmol) was added dichloromethane (2 mL). To this solution was slowly added a solution of $NaNO_2$ (34.5 mg, 0.5 mmol) in water (1 mL). The mixture was stirred at room temperature for 15 min, and then solid $NaNO_2$ (4 equiv., 1 equiv. every 15 min) was added portionwise. After the final amount of $NaNO_2$ was introduced, the mixture was stirred for an additional 15 min. Aqueous NaOH (10 M, 1 mL) was then added, and the resulting mixture was heated at reflux for 1 h. The reaction was then quenched by the addition of saturated aqueous sodium thiosulfate (5 mL). The resulting mixture was further stirred and then extracted with EtOAc (3× 10 mL). The combined organic extracts were washed with water (10 mL) and brine (10 mL). The organic layer was dried with anhydrous $MgSO_4$ and concentrated under reduced pressure. The residue was purified by column chromatography (hexanes/acetone).

General Procedure C – Two-Step Synthesis of Nitro Olefins: To a mixture of the alkene (0.5 mmol), Oxone® (368.9 mg, 1.2 mmol), and KI (83.5 mg, 1.0 mmol) was added dichloromethane (2 mL). To this solution was slowly added a solution of $NaNO_2$ (34.5 mg, 0.5 mmol) in water (1 mL). The mixture was stirred at room temperature for 15 min, and then solid $NaNO_2$ (4 equiv., 1 equiv. every 15 min) was added portionwise. After the final amount of $NaNO_2$ was introduced, the mixture was stirred for an additional 15 min. Solid $LiOH{\cdot}H_2O$ (209.8 mg, 5.0 mmol) was then added, and the

resulting mixture was heated at reflux for 1 h. The reaction was then quenched by the addition of saturated aqueous sodium thiosulfate (5 mL). The resulting mixture was further stirred and then extracted with EtOAc (3 × 10 mL). The combined organic extracts were washed with water (10 mL) and brine (10 mL). The organic layer was dried with anhydrous $MgSO_4$ and concentrated under reduced pressure. The residue was purified by column chromatography (hexanes/acetone).

(*E*)-1-Bromo-4-(2-nitrovinyl)benzene (2a):[9e] 4-Bromostyrene (**1a**, 92.3 mg, 0.5 mmol) and $NaNO_2$ (172.5 mg, 2.5 mmol) were employed as described in general procedure A. Purification by column chromatography (SiO_2, 10% acetone in hexanes) gave **2a** (102.5 mg, 88% yield) as a yellow solid, m.p. 153–154 °C; ref.[9e] m.p. 152–153 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.94 (d, J = 13.7 Hz, 1 H, CH), 7.61–7.56 (m, 3 H, ArH, CH), 7.42 (dt, J = 8.5, 2.1 Hz, 2 H, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 137.8 (CH), 137.4 (CH), 132.7 (2 CH), 130.4 (2 CH), 128.9 (C), 126.8 (C) ppm. IR (KBr): $\tilde{\nu}$ = 3105, 1635, 1587, 1519, 1501, 1336 cm^{-1}. HRMS (ESI-TOF): calcd. for $C_8H_6BrNNaO_2$ [M + Na]$^+$ 249.9480; found 249.9477.

(*E*)-1-Chloro-4-(2-nitrovinyl)benzene (2b):[9g] 4-Chlorostyrene (**1b**, 69.3 mg, 0.5 mmol) and $NaNO_2$ (172.5 mg, 2.5 mmol) were employed as described in general procedure A. Purification by column chromatography (SiO_2, 10% acetone in hexanes) gave **2b** (73.4 mg, 80% yield) as a yellow solid, m.p. 109–110 °C; ref.[9g] m.p. 110–111 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.97 (d, J = 13.7 Hz, 1 H, CH), 7.57 (d, J = 13.7 Hz, 1 H, CH), 7.50 (d, J = 8.5 Hz, 2 H, ArH), 7.44 (d, J = 8.5 Hz, 2 H, ArH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 138.3 (C), 137.6 (CH), 137.4 (CH), 130.2 (2 CH), 129.7 (2 CH), 128.5 (C) ppm. IR (KBr): $\tilde{\nu}$ = 3105, 1634, 1593, 1519, 1490, 1339 cm^{-1}. HRMS (ESI-TOF): calcd. for $C_8H_6ClNNaO_2$ [M + Na]$^+$ 205.9985; found 205.9986.

(*E*)-1-Chloro-3-(2-nitrovinyl)benzene (2c):[17a] 3-Chlorostyrene (**1c**, 69.3 mg, 0.5 mmol) and $NaNO_2$ (172.5 mg, 2.5 mmol) were employed as described in general procedure B. Purification by column chromatography (SiO_2, 10% acetone in hexanes) gave **2c** (79.9 mg, 87% yield) as a yellow viscous oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.95 (d, J = 13.7 Hz, 1 H, CH), 7.61–7.54 (m, 2 H, ArH, CH), 7.51–7.39 (m, 3 H, ArH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 138.1 (CH), 137.4 (CH), 135.4 (C), 131.9 (CH), 131.8 (C), 130.6 (CH), 128.7 (CH), 127.2 (CH) ppm. IR (neat): $\tilde{\nu}$ = 3110, 1639, 1568, 1520, 1474, 1345 cm^{-1}. HRMS (ESI-TOF): calcd. for $C_8H_6ClNNaO_2$ [M + Na]$^+$ 205.9985; found 205.9986.

(*E*)-1-Chloro-2-(2-nitrovinyl)benzene (2d):[9e] 2-Chlorostyrene (**1d**, 69.3 mg, 0.5 mmol) and $NaNO_2$ (172.5 mg, 2.5 mmol) were employed as described in general procedure B. Purification by column chromatography (SiO_2, 10% acetone in hexanes) gave **2d** (76.2 mg, 83% yield) as a yellow viscous oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.40 (d, J = 13.7 Hz, 1 H, CH), 7.62–7.57 (m, 2 H, ArH, CH), 7.50 (br. dd, J = 8.0, 1.5 Hz, 1 H, ArH), 7.43 (td, J = 7.2, 1.7 Hz, 1 H, ArH), 7.34 (br. td, J = 8.7, 1.6 Hz, 1 H, ArH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 138.8 (CH), 136.0 (C), 135.1 (CH), 132.8 (CH), 130.7 (CH), 128.6 (CH), 128.4 (C), 127.4 (CH) ppm. IR (neat): $\tilde{\nu}$ = 3112, 1634, 1591, 1526, 1471, 1443, 1340 cm^{-1}. HRMS (ESI-TOF): calcd. for $C_8H_6ClNNaO_2$ [M + Na]$^+$ 205.9985; found 205.9991.

(*E*)-1-Fluoro-4-(2-nitrovinyl)benzene (2e):[17b] 4-Fluorostyrene (**1e**, 61.1 mg, 0.5 mmol) and $NaNO_2$ (172.5 mg, 2.5 mmol) were employed as described in general procedure A. Purification by column chromatography (SiO_2, 10% acetone in hexanes) gave **2e** (66.9 mg, 80% yield) as a yellow solid, m.p. 102–103 °C; ref.[17b] m.p. 100 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.98 (d, J = 13.7 Hz, 1 H, CH), 7.59–7.52 (m, 3 H, ArH, CH), 7.18–7.13 (m, 2 H, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 164.9 (d, J = 253.0 Hz, C), 137.8 (CH), 136.8 (CH), 131.3 (d, J = 9.0 Hz, 2 CH), 126.3 (C), 116.8 (d, J = 22.0 Hz, 2 CH) ppm. IR (KBr): $\tilde{\nu}$ = 3113, 3047, 1637, 1595, 1504, 1415, 1346 cm^{-1}. HRMS (ESI-TOF): calcd. for $C_8H_6FNNaO_2$ [M + Na]$^+$ 190.0280; found 190.0273.

(*E*)-1-Fluoro-3-(2-nitrovinyl)benzene (2f):[17c] 3-Fluorostyrene (**1f**, 61.1 mg, 0.5 mmol) and $NaNO_2$ (172.5 mg, 2.5 mmol) were employed as described in general procedure B. Purification by column chromatography (SiO_2, 10% acetone in hexanes) gave **2f** (69.6 mg, 82% yield) as a yellow viscous oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.88 (d, J = 13.7 Hz, 1 H, CH), 7.48 (d, J = 13.7 Hz, 1 H, CH), 7.40–7.33 (m, 1 H, ArH), 7.28–7.25 (m, 1 H, ArH), 7.19–7.09 (m, 2 H, ArH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 162.9 (d, J = 247.2 Hz, C), 138.1 (CH), 137.6 (d, J = 2.8 Hz, CH), 132.1 (d, J = 7.9 Hz, C), 131.0 (d, J = 8.3 Hz, CH), 125.1 (d, J = 3.0 Hz, CH), 119.0 (d, J = 21.2 Hz, CH), 115.4 (d, J = 22.3 Hz, CH) ppm. IR (neat): $\tilde{\nu}$ = 3111, 1641, 1584, 1520, 1448, 1347 cm^{-1}. HRMS (ESI-TOF): calcd. for $C_8H_6FNNaO_2$ [M + Na]$^+$ 190.0280; found 190.0287.

(*E*)-(2-Nitrovinyl)benzene (2g):[9g] Styrene (**1g**, 52.1 mg, 0.5 mmol) and $NaNO_2$ (172.5 mg, 2.5 mmol) were employed as described in general procedure B. Purification by column chromatography (SiO_2, 10% acetone in hexanes) gave **2g** (55.9 mg, 75% yield) as a yellow solid, m.p. 59–60 °C; ref.[9g] m.p. 55–58 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.01 (d, J = 13.7 Hz, 1 H, CH), 7.59 (d, J = 13.7 Hz, 1 H, CH), 7.56–7.43 (m, 5 H, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 139.0 (CH), 137.1 (CH), 132.1 (CH), 130.0 (C), 129.4 (2 CH), 129.1 (2 CH) ppm. IR (KBr): $\tilde{\nu}$ = 3110, 1633, 1578, 1515, 1449, 1343 cm^{-1}. HRMS (ESI-TOF): calcd. for $C_8H_8NO_2$ [M + H]$^+$ 150.0555; found 150.0560.

(*E*)-1-Nitro-4-(2-nitrovinyl)benzene (2h):[17d] 4-Nitrostyrene (**1h**, 74.5 mg, 0.5 mmol) and $NaNO_2$ (172.5 mg, 2.5 mmol) were employed as described in general procedure A. Purification by column chromatography (SiO_2, 10% acetone in hexanes) gave **2h** (51.5 mg, 53% yield) as a yellow solid, m.p. 109–110 °C; ref.[17d] m.p. 106–107 °C. ^{1}H NMR (300 MHz, [D$_6$]acetone): δ = 8.32 (dt, J = 9.0, 2.3 Hz, 2 H, ArH), 8.22–8.08 (m, 4 H, ArH, CH) ppm. ^{13}C NMR (75 MHz, [D$_6$]acetone): δ = 150.3 (C), 141.5 (CH), 137.7 (C), 137.0 (CH), 131.3 (2 CH), 124.9 (2 CH) ppm. IR (KBr): $\tilde{\nu}$ = 3112, 1604, 1535, 1494, 1466, 1346 cm^{-1}. HRMS (ESI-TOF): calcd. for $C_8H_6N_2NaO_4$ [M + Na]$^+$ 217.0225; found 217.0219.

(*E*)-1-Nitro-3-(2-nitrovinyl)benzene (2i):[17b] 3-Nitrostyrene (**1i**, 74.5 mg, 0.5 mmol) and $NaNO_2$ (172.5 mg, 2.5 mmol) were employed as described in general procedure A. Purification by column chromatography (SiO_2, 10% acetone in hexanes) gave **2i** (67.0 mg, 69% yield) as a yellow solid, m.p. 120–121 °C; ref,[17b] m.p. 125 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.44 (s, 1 H, ArH), 8.37 (d, J = 8.4 Hz, 1 H, ArH), 8.07 (d, J = 13.7 Hz, 1 H, CH), 7.90 (d, J = 7.6 Hz, 1 H, ArH), 7.73–7.67 (m, 2 H, ArH, CH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 148.8 (C), 139.3 (CH), 136.2 (CH), 134.4 (CH), 131.8 (C), 130.6 (CH), 126.2 (CH), 123.4 (CH) ppm. IR (KBr): $\tilde{\nu}$ = 3104, 1530, 1509, 1440, 1350 cm^{-1}. HRMS (ESI-TOF): calcd. for $C_8H_6N_2NaO_4$ [M + Na]$^+$ 217.0225; found 217.0227.

(*E*)-3-(2-Nitrovinyl)benzaldehyde (2j):[9e] 3-Vinylbenzaldehyde (**1j**, 66.1 mg, 0.5 mmol) and $NaNO_2$ (172.5 mg, 2.5 mmol) were employed as described in general procedure A. Purification by column chromatography (SiO_2, 10% acetone in hexanes) gave **2j** (60.2 mg, 68% yield) as a yellow solid, m.p. 91–92 °C; ref,[9e] m.p. 90 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 10.00 (s, 1 H, CHO), 8.01–7.92 (m, 3 H, ArH, CH), 7.74 (d, J = 7.8 Hz, 1 H, ArH), 7.62–7.57 (m, 2 H, ArH, CH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 191.0 (CH),

138.4 (CH), 137.4 (CH), 137.2 (C), 134.3 (CH), 132.8 (CH), 131.1 (C), 130.2 (CH), 129.5 (CH) ppm. IR (KBr): $\tilde{\nu}$ = 3111, 1640, 1578, 1526, 1493, 1445, 1350 cm^{-1}. HRMS (ESI-TOF): calcd. for $C_9H_7NNaO_3$ $[M + Na]^+$ 200.0324; found 200.0332.

(*E*)-1-(Chloromethyl)-4-(2-nitrovinyl)benzene (2k):[9e] 4-Vinylbenzyl chloride (**1k**, 76.3 mg, 0.5 mmol) and $NaNO_2$ (172.5 mg, 2.5 mmol) were employed as described in general procedure B. Purification by column chromatography (SiO_2, 10% acetone in hexanes) gave **2k** (72.6 mg, 73% yield) as a yellow solid, m.p. 105–106 °C; ref.[9e] m.p. 107–108 °C. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.9 (d, J = 13.7 Hz, 1 H, CH), 7.53–7.46 (m, 3 H, ArH, CH), 7.40 (d, J = 8.3 Hz, 2 H, ArH), 4.53 (s, 2 H, CH_2) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 141.5 (C), 138.1 (CH), 137.5 (CH), 130.1 (C), 129.5 (2 CH), 129.4 (2 CH), 45.2 (CH_2) ppm. IR (KBr): $\tilde{\nu}$ = 3116, 1637, 1569, 1501, 1445, 1347 cm^{-1}. HRMS (ESI-TOF): calcd. for $C_9H_8ClNNaO_2$ $[M + Na]^+$ 220.0141; found 220.0142.

(*E*)-4-(2-Nitrovinyl)phenyl Acetate (2l):[7f] 4-Acetoxystyrene (**1l**, 81.1 mg, 0.5 mmol) and $NaNO_2$ (172.5 mg, 2.5 mmol) were employed as described in general procedure A. Purification by column chromatography (SiO_2, 10% acetone in hexanes) gave **2l** (64.2 mg, 62% yield) as a yellow solid; m.p. 147–148 °C. ^1H NMR (300 MHz, $CDCl_3$): δ = 8.00 (d, J = 13.7 Hz, 1 H, CH), 7.60–7.53 (m, 3 H, ArH, CH), 7.21 (d, J = 8.4 Hz, 2 H, ArH), 2.33 (s, 3 H, CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 168.8 (C), 153.5 (C), 138.0 (CH), 137.1 (CH), 130.4 (2 CH), 127.6 (C), 122.8 (2 CH), 21.1 (CH_3) ppm. IR (KBr): $\tilde{\nu}$ = 3106, 1746, 1603, 1561, 1502, 1349 cm^{-1}. MS: *m*/*z* (%) = 207 (3) $[M]^+$, 165 (51), 148 (8), 118 (100), 89 (25). HRMS (ESI-TOF): calcd. for $C_{10}H_9NNaO_4$ $[M + Na]^+$ 230.0429; found 230.0441.

(*E*)-1-(*tert*-Butyl)-4-(2-nitrovinyl)benzene (2m): 4-*tert*-Butylstyrene (**1m**, 80.1 mg, 0.5 mmol) and $NaNO_2$ (172.5 mg, 2.5 mmol) were employed as described in general procedure B. Purification by column chromatography (SiO_2, 10% acetone in hexanes) gave **2m** (35.9 mg, 35% yield) as a yellow viscous oil. ^1H NMR (400 MHz, $CDCl_3$): δ = 8.00 (d, J = 13.7 Hz, 1 H, CH), 7.58 (d, J = 13.7 Hz, 1 H, CH), 7.50 (d, J = 8.9 Hz, 2 H, ArH), 7.47 (d, J = 8.9 Hz, 2 H, ArH), 1.34 (s, 9 H, 3 CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 156.2 (C), 139.1 (CH), 136.4 (CH), 129.1 (2 CH), 127.2 (C), 126.4 (2 CH), 35.1 (C), 31.0 (3 CH_3) ppm. IR (neat): $\tilde{\nu}$ = 3109, 2964, 1633, 1606, 1521, 1464, 1415, 1338 cm^{-1}. MS: *m*/*z* (%) = 205 (1) $[M]^+$, 190 (16), 160 (11), 143 (57), 128 (49), 115 (100), 103 (20), 91 (25). HRMS (ESI-TOF): calcd. for $C_{12}H_{15}NNaO_2$ $[M + Na]^+$ 228.1000; found 228.0997.

(*E*)-(2-Nitroprop-1-en-1-yl)benzene (2n):[17b] *trans*-β-Methylstyrene (**1n**, 59.1 mg, 0.5 mmol) and $NaNO_2$ (172.5 mg, 2.5 mmol) were employed as described in general procedure B. Purification by preparative thin layer chromatography (SiO_2, 2% EtOAc in hexanes) gave **2n** (55.2 mg, 68% yield) as a yellow solid, m.p. 62–63 °C; ref.[17b] m.p. 62 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 8.09 (s, 1 H, CH), 7.46–7.42 (m, 5 H, ArH), 2.46 (d, J = 0.8 Hz, 3 H, CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 147.8 (C), 133.5 (CH), 132.4 (C), 130.0 (2 CH), 129.9 (CH), 128.9 (2 CH), 14.0 (CH_3) ppm. IR (KBr): $\tilde{\nu}$ = 3058, 2925, 1519, 1449, 1387, 1324 cm^{-1}. HRMS (ESI-TOF): calcd. for $C_9H_9NNaO_2$ $[M + Na]^+$ 186.0531; found 186.0520.

(*E*)-1-(2-Nitrovinyl)naphthalene (2o):[9g] 1-Vinylnaphthalene (**1o**, 77.1 mg, 0.5 mmol) and $NaNO_2$ (172.5 mg, 2.5 mmol) were employed as described in general procedure B. Purification by column chromatography (SiO_2, 10% acetone in hexanes) gave **2o** (41.8 mg, 42% yield) as a yellow solid, m.p. 85–87 °C; ref.[9g] m.p. 84–86 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 8.84 (d, J = 13.4 Hz, 1 H, CH), 8.14 (d, J = 8.2 Hz, 1 H, ArH), 8.01 (d, J = 8.2 Hz, 1 H, ArH), 7.93 (d, J = 7.5 Hz, 1 H, ArH), 7.75 (d, J = 7.2 Hz, 1 H, ArH), 7.67–7.56 (m, 3 H, ArH, CH), 7.52 (t, J = 7.8 Hz, 1 H, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 138.5 (CH), 136.1 (CH), 133.7 (C), 132.5 (CH), 131.5 (C), 129.0 (CH), 127.7 (CH), 127.0 (C), 126.8 (CH), 126.4 (CH), 125.4 (CH), 122.9 (CH) ppm. IR (KBr): $\tilde{\nu}$ = 3111, 1632, 1505, 1395, 1339 cm^{-1}. HRMS (ESI-TOF): calcd. for $C_{12}H_9NNaO_2$ $[M + Na]^+$ 222.0531; found 222.0528.

(*E*)-[(3-Nitroallyl)oxy]benzene (2p):[7n] Allyl phenyl ether (**1p**, 67.6 mg, 0.5 mmol) and $NaNO_2$ (172.5 mg, 2.5 mmol) were employed as described in general procedure C. Purification by column chromatography (SiO_2, 5% acetone in hexanes) gave **2p** (20.6 mg, 23% yield) as a yellow viscous oil. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.41 (dt, J = 13.3, 3.4 Hz, 1 H, CH), 7.35–7.31 (m, 3 H, ArH), 7.04 (t, J = 7.4 Hz, 1 H, CH), 6.93 (dd, J = 8.8, 0.9 Hz, 2 H, ArH), 4.81 (dd, J = 3.3, 2 Hz, 2 H, CH_2) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.4 (C), 140.3 (CH), 136.7 (CH), 129.8 (2 CH), 122.0 (CH), 114.5 (2 CH), 63.6 (CH_2) ppm. IR (neat): $\tilde{\nu}$ = 3131, 2909, 1589, 1534, 1492, 1437, 1362 cm^{-1}. HRMS (ESI-TOF): calcd. for $C_9H_9NNaO_3$ $[M + Na]^+$ 202.0480; found 202.0479.

(*E*)-[(5-Nitropent-4-en-1-yl)oxy]benzene (2q): (Pent-4-en-1-yloxy)-benzene (**1q**, 72.1 mg, 0.5 mmol) and $NaNO_2$ (172.5 mg, 2.5 mmol) were employed as described in general procedure C. Purification by column chromatography (SiO_2, 5% acetone in hexanes) gave **2q** (26.9 mg, 26% yield) as a yellow viscous oil. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.38–7.27 (m, 3 H, ArH, CH), 7.03 (dt, J = 13.4, 1.5 Hz, 1 H, CH), 6.96 (t, J = 7.4 Hz, 1 H, ArH), 6.89 (dd, J = 8.8, 1.0 Hz, 2 H, ArH), 4.02 (t, J = 5.8 Hz, 2 H, CH_2), 2.51 (ddd, J = 14.8, 7.3, 1.5 Hz, 2 H, CH_2), 2.05–1.98 (m, 2 H, CH_2) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.5 (C), 141.8 (CH), 139.9 (CH), 129.6 (2 CH), 121.0 (CH), 114.4 (2 CH), 66.3 (CH_2), 27.6 (CH_2), 25.4 (CH_2) ppm. IR (neat): $\tilde{\nu}$ = 3103, 3041, 2930, 1600, 1587, 1524, 1497, 1355 cm^{-1}. MS: *m*/*z* (%) = 207 (98) $[M]^+$, 161 (33), 94 (100), 77 (21), 63 (54). HRMS (ESI-TOF): calcd. for $C_{11}H_{13}NNaO_3$ $[M + Na]^+$ 230.0793; found 230.0795.

(*E*)-(3-Nitroallyl)benzene (2r):[17e] Allylbenzene (**1r**) (59.1 mg, 0.5 mmol) and $NaNO_2$ (172.5 mg, 2.5 mmol) were employed as described in general procedure C. Purification by column chromatography (SiO_2, 2% acetone in hexanes) gave **2q** (27.7 mg, 34% yield) as a yellow viscous oil. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.46–7.28 (m, 4 H, ArH, CH), 7.19 (br. d, J = 7.6 Hz, 2 H, ArH), 6.92 (dt, J = 13.3, 1.7 Hz, 1 H, CH), 3.59 (dd, J = 7.0, 1.4 Hz, 2 H, CH_2) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 141.0 (CH), 140.4 (CH), 135.7 (C), 129.1 (2 CH), 128.7 (2 CH), 127.4 (CH), 34.6 (CH_2) ppm. IR (KBr): $\tilde{\nu}$ = 3105, 2923, 1524, 1496, 1454, 1353 cm^{-1}. HRMS (ESI-TOF): calcd. for $C_9H_9NNaO_2$ $[M + Na]^+$ 186.0531; found 186.0532.

6-Nitro-1-phenylcyclohexene (2s):[17f] 1-Phenylcyclohexene (**1s**, 79.1 mg, 0.5 mmol) and $NaNO_2$ (172.5 mg, 2.5 mmol) were employed as described in general procedure C. Purification by column chromatography (SiO_2, 5% acetone in hexanes) gave **2s** (47.8 mg, 47% yield) as a yellow viscous oil. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.43–7.16 (m, 5 H, ArH), 6.39 (t, J = 4.1 Hz, 1 H, CH), 5.53 (t, J = 4.6 Hz, 1 H, CH), 2.44–2.32 (m, 2 H, CH_2), 2.25–2.07 (m, 2 H, CH_2), 1.80–1.65 (m, 2 H, CH_2) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 138.8 (C), 133.8 (CH), 131.3 (C), 128.6 (2 CH), 127.7 (CH), 125.5 (2 CH), 83.0 (CH), 29.0 (CH_2), 25.4 (CH_2), 17.3 (CH_2) ppm. IR (neat): $\tilde{\nu}$ = 3058, 2940, 1547, 1496, 1446, 1374 cm^{-1}. HRMS (ESI-TOF): calcd. for $C_{12}H_{13}NNaO_2$ $[M + Na]^+$ 226.0844; found 226.0839.

***tert*-Butyl (*E*)-3-Nitroacrylate (2t):** *tert*-Butyl acrylate (**1t**, 64.1 mg, 0.5 mmol) and $NaNO_2$ (172.5 mg, 2.5 mmol) were employed as described in general procedure C. Purification by column chromatog-

raphy (SiO_2, 5% acetone in hexanes) gave **2t** (13.9 mg, 16% yield) as a yellow viscous oil. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.59 (d, J = 13.5 Hz, 1 H, CH), 7.01 (d, J = 13.5 Hz, 1 H, CH), 1.53 (s, 9 H, 3 CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.7 (C), 148.4 (CH), 129.5 (CH), 83.8 (C), 27.9 (3 CH_3) ppm. IR (neat): $\tilde{\nu}$ = 2925, 2854, 1733, 1564, 1372 cm^{-1}. MS: m/z (%) = 173 (3) $[M]^+$, 148 (100), 147 (20), 121 (13). HRMS (ESI-TOF): calcd. for $C_7H_{11}NNaO_4$ $[M + Na]^+$ 196.0586; found 196.0586.

(1-Iodo-2-nitrovinyl)benzene (5a):[14c] Phenylacetylene (**4a**, 51.0 mg, 0.5 mmol) and $NaNO_2$ (172.5 mg, 2.5 mmol) were employed as described in general procedure A. Purification by column chromatography (SiO_2, 5% acetone in hexanes) gave a mixture of the (*E*) and (*Z*) isomers (i.e., A and B, respectively) of **5a** (86.8 mg, 62% yield. *E*/*Z*, 5.6:1) as a yellow viscous oil. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.74 (s, 1 H of A, CH), 7.67 (s, 1 H of B, CH), 7.53 (dd, J = 7.4, 1.6 Hz, 2 H of B, ArH), 7.44–7.30 (m, 8 H of A, B, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 143.2 (CH, B), 142.9 (CH, A), 138.5 (2 C, A, B), 131.2 (CH, B), 130.2 (CH, A), 129.1 (2 CH, B), 128.9 (2 CH, B), 128.5 (2 CH, A), 127.3 (2 CH, A), 113.8 (2 C, A, B) ppm. IR (KBr): $\tilde{\nu}$ = 3101, 1592, 1525, 1488, 1444, 1335, 961, 692 cm^{-1}. HRMS (ESI-TOF): calcd. for $C_8H_6INNaO_2$ $[M + Na]^+$ 297.9341; found 297.9334.

1-(1-Iodo-2-nitrovinyl)-4-methylbenzene (5b): 4-Ethynyltoluene (**4b**, 58.1 mg, 0.5 mmol) and $NaNO_2$ (172.5 mg, 2.5 mmol) were employed as described in general procedure A. Purification by column chromatography (SiO_2, 5% acetone in hexanes) gave a mixture of the (*E*) and (*Z*) isomers (i.e., A and B, respectively) of **5b** (104.5 mg, 70% yield; *E*/*Z*, 4.8:1) as a yellow solid; m.p. 55–57 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.64 (s, 1 H of A, CH), 7.59 (s, 1 H of B, ArH), 7.36 (d, J = 8.2 Hz, 2 H of B, ArH), 7.18–7.10 (m, 6 H of A, B, ArH), 2.33 (s, 3 H of B, CH_3), 2.30 (s, 3 H of A, CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 142.5 (2 CH, A, B), 140.8 (2 C, A, B), 135.5 (2 C, A, B), 129.6 (2 CH, B), 129.2 (2 CH, A), 129.1 (2 CH, B), 127.5 (2 CH, A), 114.5 (2 C, A, B), 21.4 (CH_3, A), 21.3 (CH_3, B) ppm. IR (KBr): $\tilde{\nu}$ = 3099, 1604, 1520, 1501, 1333, 811 cm^{-1}. MS: m/z (%) = 289 (2) $[M]^+$, 162 (16), 119 (29), 115 (100), 91 (25), 89 (22). HRMS (ESI-TOF): calcd. for $C_9H_8INNaO_2$ $[M + Na]^+$ 311.9497; found 311.9508.

1-(1-Iodo-2-nitrovinyl)-4-methoxybenzene (5c): 4-Ethynylanisole (**4c**, 66.1 mg, 0.5 mmol) and $NaNO_2$ (172.5 mg, 2.5 mmol) were employed as described in general procedure A. Purification by preparative thin layer chromatography (SiO_2, 3% acetone in hexanes) gave a mixture of the (*E*) and (*Z*) isomers (i.e., A and B, respectively) of **5c** (30.5 mg, 20% yield; *E*/*Z*, 4.2:1) as a yellow viscous oil. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.71 (s, 1 H of A, CH), 7.66 (s, 1 H of B, CH), 7.52 (d, J = 8.8 Hz, 2 H of B, ArH), 7.31 (d, J = 8.8 Hz, 2 H of A, ArH), 6.93–6.87 (m, 4 H of A, B, ArH), 3.86 (s, 3 H of B, CH_3), 3.84 (s, 3 H of A, CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.2 (2 C, A, B), 142.0 (CH, A), 141.7 (CH, B), 131.0 (2 CH, B), 130.2 (2 C, A, B), 129.9 (2 CH, A), 114.9 (2 C, A, B), 114.3 (2 CH, B), 113.8 (2 CH, A), 55.6 (CH_3, B), 55.4 (CH_3, A) ppm. IR (neat): $\tilde{\nu}$ = 3068, 2929, 1603, 1525, 1503, 1462, 1328, 1254 cm^{-1}. MS: m/z (%) = 305 (11) $[M]^+$, 135 (100), 132 (62), 89 (26). HRMS [atmospheric pressure chemical ionization (APCI)-TOF]: calcd. for $C_9H_9INO_3$ $[M + H]^+$ 305.9627; found 305.9622.

1-Bromo-4-(1-iodo-2-nitrovinyl)benzene (5d): 1-Bromo-4-ethynylbenzene (**4d**, 90.5 mg, 0.5 mmol) and $NaNO_2$ (172.5 mg, 2.5 mmol) were employed as described in general procedure A. Purification by column chromatography (SiO_2, 5% acetone in hexanes) gave a mixture of the (*E*) and (*Z*) isomers (i.e., A and B, respectively) of **5d** (111.5 mg, 63% yield; *E*/*Z*, 6.7:1) as a yellow solid; m.p. 95–96 °C. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.73 (s, 1 H of A, CH), 7.70 (s, 1 H of B, CH), 7.57–7.50 (m, 4 H of A, B, ArH), 7.40 (dt, J = 8.7, 2.0 Hz, 2 H of B, ArH), 7.18 (dt, J = 8.7, 2.4 Hz, 2 H of A, ArH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 143.3 (2 CH, A, B), 138.2 (C, B), 137.3 (C, A), 132.1 (2 CH, B), 131.8 (2 CH, A), 130.4 (2 CH, B), 128.8 (2 CH, A), 125.9 (C, B), 124.6 (C, A), 112.2 (2 C, A, B) ppm. IR (KBr): $\tilde{\nu}$ = 3100, 1604, 1516, 1482, 1395, 1330, 815 cm^{-1}. MS: m/z (%) = 353 (11) $[M]^+$, 274 (10), 183 (90), 180 (58), 75 (100), 74 (79). HRMS (APCI-TOF): calcd. for $C_8H_6BrINO_2$ $[M + H]^+$ 353.8627; found 353.8620.

1-Bromo-2-(1-iodo-2-nitrovinyl)benzene (5e): 1-Bromo-2-ethynylbenzene (**4e**, 90.5 mg, 0.5 mmol) and $NaNO_2$ (172.5 mg, 2.5 mmol) were employed as described in General Procedure A. Purification by column chromatography (SiO_2, 5% acetone in hexanes) gave a mixture of the (*E*) and (*Z*) isomers (i.e., A and B, respectively) of **5e** (100.9 mg, 57% yield; *E*/*Z*, 9.1:1) as a yellow solid; m.p. 56–57 °C. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.79 (s, 1 H of A, CH), 7.61 (d, J = 7.9 Hz, 2 H of A, B, ArH), 7.48 (s, 1 H of B, CH), 7.40–7.35 (m, 2 H of A, B, ArH), 7.28–7.19 (m, 4 H of A, B, ArH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 145.6 (CH, B), 144.8 (CH, A), 140.0 (C, B), 139.5 (C, A), 133.6 (CH, B), 133.2 (CH, A), 131.2 (CH, B), 130.8 (CH, A), 129.3 (CH, B), 127.7 (CH, A), 127.6 (CH, B), 127.5 (CH, A), 121.2 (C, B), 119.8 (C, A), 111.7 (2 C, A, B) ppm. IR (KBr): $\tilde{\nu}$ = 3107, 1622, 1521, 1459, 1423, 1334, 845 cm^{-1}. MS: m/z (%) = 353 (6) $[M]^+$, 273 (100), 258 (32), 244 (41). HRMS (APCI-TOF): calcd. for $C_8H_6BrINO_2$ $[M + H]^+$ 353.8627; found 353.8622.

1-Fluoro-4-(1-iodo-2-nitrovinyl)benzene (5f): 1-Ethynyl-4-fluorobenzene (**4f**, 60.0 mg, 0.5 mmol) and $NaNO_2$ (172.5 mg, 2.5 mmol) were employed as described in general procedure A. Purification by column chromatography (SiO_2, 5% acetone in hexanes) gave a mixture of the (*E*) and (*Z*) isomers (i.e., A and B, respectively) of **5f** (95.2 mg, 65% yield; *E*/*Z*, 5.9:1) as a yellow semisolid. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.73 (s, 1 H of A, CH), 7.63 (s, 1 H of B, CH), 7.56–7.51 (m, 2 H of B, ArH), 7.35–7.29 (m, 2 H of A, ArH), 7.14–7.04 (m, 4 H of A, B, ArH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 164.3 (d, J = 252.1 Hz, C, B), 163.3 (d, J = 250.7 Hz, C, A), 143.1 (2 CH, A, B), 135.4 (d, J = 3.4 Hz, C, B), 134.3 (d, J = 3.6 Hz, C, A), 131.1 (d, J = 8.8 Hz, 2 CH, B), 129.6 (d, J = 8.7 Hz, 2 CH, A), 116.0 (d, J = 20.9 Hz, 2 CH, B), 115.8 (d, J = 22.1 Hz, 2 CH, A), 112.5 (C, A), 108.7 (C, B) ppm. IR (KBr): $\tilde{\nu}$ = 3105, 1598, 1502, 1406, 1333, 1236, 893 cm^{-1}. MS: m/z (%) = 293 (1) $[M]^+$, 123 (100), 120 (72), 74 (43). HRMS (ESI-TOF): calcd. for $C_8H_5FINNaO_2$ $[M + Na]^+$ 315.9247; found 315.9247.

1-Fluoro-3-(1-iodo-2-nitrovinyl)benzene (5g): 1-Ethynyl-3-fluorobenzene (**4g**, 60.0 mg, 0.5 mmol) and $NaNO_2$ (172.5 mg, 2.5 mmol) were employed as described in general procedure A. Purification by column chromatography (SiO_2, 5% acetone in hexanes) gave a mixture of the (*E*) and (*Z*) isomers (i.e., A and B, respectively) of **5g** (70.3 mg, 48% yield; *E*/*Z*, 6.3:1) as a yellow semisolid. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.72 (s, 1 H of A, CH), 7.67 (s, 1 H of B, CH), 7.41–6.99 (m, 8 H of A, B, ArH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 162.4 (d, J = 247.7 Hz, C, B), 162.1 (d, J = 247.1 Hz, C, A), 143.8 (CH, B), 143.5 (CH, A), 141.3 (d, J = 7.8 Hz, C, B), 140.3 (d, J = 8.3 Hz, C, A), 130.5 (d, J = 8.3 Hz, CH, B), 130.3 (d, J = 8.4 Hz, CH, A), 124.5 (d, J = 3.1 Hz, CH, B), 122.8 (d, J = 3.2 Hz, CH, A), 118.1 (d, J = 21.1 Hz, CH, B), 117.2 (d, J = 21.0 Hz, CH, A), 116.5 (d, J = 23.7 Hz, CH, B), 114.5 (d, J = 23.6 Hz, CH, A), 111.1 (d, J = 2.4 Hz, C, A), 107.8 (C, B) ppm. IR (KBr): $\tilde{\nu}$ = 3103, 1583, 1527, 1482, 1434, 1335, 1228 cm^{-1}. MS: m/z (%) = 294 (100) $[M + 1]^+$, 166 (15), 134 (57), 120 (48), 107 (34). HRMS (ESI-TOF): calcd. for $C_8H_5FINNaO_2$ $[M + Na]^+$ 315.9247; found 315.9257.

1-(1-Iodo-2-nitrovinyl)-4-nitrobenzene (5h): 1-Ethynyl-4-nitrobenzene (**4h**, 73.6 mg, 0.5 mmol) and $NaNO_2$ (172.5 mg, 2.5 mmol) were employed as described in general procedure A. Purification by column chromatography (SiO_2, 5% acetone in hexanes) gave a mixture of the (*E*) and (*Z*) isomers (i.e., A and B, respectively) of **5h** (41.6 mg, 26% yield; *E*/*Z*, 3.4:1) as a yellow solid; m.p. 114–116 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 8.30–8.25 (m, 4 H of A, B, ArH), 7.79 (s, 1 H of A, CH), 7.70 (d, J = 8.1 Hz, 2 H of B, ArH), 7.46 (dt, J = 8.8, 2.2 Hz, 3 H of A, B, ArH, CH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 148.2 (2 C, A, B), 145.0 (2 C, A, B), 144.8 (CH, B), 144.3 (CH, A), 129.9 (2 CH, B), 128.0 (2 CH, A), 124.0 (2 CH, B), 123.9 (2 CH, A), 109.8 (2 C, A, B) ppm. IR (KBr): $\tilde{\nu}$ = 3111, 1586, 1524, 1514, 1402, 1343, 1316, 833 cm^{-1}. MS: *m*/*z* (%) = 320 (1) $[M]^+$, 304 (26), 273 (20), 191 (36), 150 (28), 119 (53), 92 (82), 75 (100). HRMS (ESI-TOF): calcd. for $C_8H_5IN_2NaO_4$ $[M + Na]^+$ 342.9192; found 342.9183.

(1-Iodo-2-nitroprop-1-en-1-yl)benzene (5i): (Prop-1-yn-1-yl)benzene (**4i**, 58.1 mg, 0.5 mmol) and $NaNO_2$ (172.5 mg, 2.5 mmol) were employed as described in general procedure A. Purification by column chromatography (SiO_2, 5% acetone in hexanes) gave a mixture of the (*E*) and (*Z*) isomers (i.e., A and B, respectively) of **5i** (77.0 mg, 53% yield; *E*/*Z*, 4.7:1) as a yellow viscous oil. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.40–7.24 (m, 10 H of A, B, ArH), 2.62 (s, 3 H of A, CH_3), 2.16 (s, 3 H of B, CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 151.1 (2 C, A, B), 142.9 (C, B), 140.1 (C, B), 129.4 (CH, A), 129.3 (CH, B), 128.7 (2 CH, B), 128.6 (2 CH, A), 128.1 (2 CH, B), 127.3 (2 CH, A), 103.5 (2 C, A, B), 24.4 (CH_3, A), 18.3 (CH_3, B) ppm. IR (KBr): $\tilde{\nu}$ = 3057, 2922, 1523, 1488, 1442, 1378, 1334 cm^{-1}. MS: *m*/*z* (%) = 289 (1) $[M]^+$, 272 (7), 162 (19), 115 (100), 105 (72). HRMS (ESI-TOF): calcd. for $C_9H_8INNaO_2$ $[M + Na]^+$ 311.9497; found 311.9496.

(*E*)-1-(1,2-Diiodovinyl)-4-methoxybenzene (6): 4-Ethynylanisole (**4c**, 66.1 mg, 0.5 mmol) and $NaNO_2$ (172.5 mg, 2.5 mmol) were employed as described in general procedure A. Purification by preparative thin layer chromatography (SiO_2, 3% acetone in hexanes) gave **6** (57.9 mg, 30% yield) as a yellow solid; m.p. 40 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.34 (d, J = 8.8 Hz, 2 H, ArH), 7.20 (s, 1 H, CH), 6.88 (d, J = 8.8 Hz, 2 H, ArH), 3.83 (s, 3 H, CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.7 (C), 135.2 (C), 130.2 (2 CH), 113.6 (2 CH), 96.6 (C), 79.8 (CH), 55.3 (CH_3) ppm. IR (KBr): $\tilde{\nu}$ = 3057, 2924, 1604, 1503, 1465, 1296, 1255 cm^{-1}. MS: *m*/*z* (%) = 386 (100) $[M]^+$, 260 (20), 133 (7). HRMS (ESI-TOF): calcd. for $C_9H_9I_2O$ $[M + H]^+$ 386.8743; found 386.8759.

Supporting Information (see footnote on the first page of this article): NOE data for **5b** and copies of ^1H and ^{13}C NMR spectra of all reported compounds.

Acknowledgments

The authors thank the Thailand Research Fund (TRF-DBG5480017), the Center of Excellence for Innovation in Chemistry (PERCH-CIC), the Office of the Higher Education Commission, Mahidol University under the National Research Universities Initiative and the Development and Promotion of Science and Technology Talent Project (DPST), and the Institute for the Promotion of Teaching Science and Technology for financial support.

[1] a) G. G. Graboski, A. G. M. Berrett, *Chem. Rev.* **1986**, *86*, 751–762; b) H. Feuer, A. T. Nielsen (Eds.), *Nitro Compounds: Recent Advances in Synthesis and Chemistry*, VCH, New York, **1990**; c) H. Uehara, R. Imashiro, G. Hernandez-Torres, C. F. Barbas III, *Proc. Natl. Acad. Sci. U.S.A.* **2010**, *107*, 20672–20677; d) M. A. Reddy, N. Jain, D. Yada, C. Kishore, V. J. Reddy, P. S. Reddy, A. Addlagatta, S. V. Kalivendi, B. Sreedhar, *J. Med. Chem.* **2011**, *54*, 6751–6760; e) L. Q. Lu, J. R. Chen, W. Xiao, *Acc. Chem. Res.* **2012**, *45*, 1278–1293.

[2] a) D. J. P. Bates, M. O. Lively, M. J. Gorczynski, S. B. King, A. J. Townsend, C. S. Morrow, *Biochemistry* **2009**, *48*, 4159–4169; b) L. Villacorta, F. J. Schopfer, J. Zhang, B. A. Freeman, Y. E. Chen, *Clin. Sci.* **2009**, *116*, 205–218.

[3] a) G. H. Posner, R. D. Crouch, *Tetrahedron* **1990**, *46*, 7509–7530; b) N. Mase, K. Watanabe, H. Yoda, K. Takabe, F. Tanaka, C. F. Barbas III, *J. Am. Chem. Soc.* **2006**, *128*, 4966–4967.

[4] a) A. G. M. Barrett, *Chem. Soc. Rev.* **1991**, *20*, 95–127; b) E. Ghera, T. Yechezkel, A. Hassner, *J. Org. Chem.* **1993**, *58*, 6716–6724.

[5] a) C. Palomo, J. M. Aizpurua, F. P. Cossio, J. M. Garcia, M. C. Lopez, M. Oiarbide, *J. Org. Chem.* **1990**, *55*, 2070–2078; b) R. Ballini, M. Petrini, *Tetrahedron* **2004**, *60*, 1017–1047; c) J. R. Hwu, T. Josephrajan, S.-C. Tsay, *Synthesis* **2006**, 3305–3308; d) A. Corma, P. Serna, H. Garcia, *J. Am. Chem. Soc.* **2007**, *129*, 6358–6359; e) D. P. Gavin, J. C. Stephens, *ARKIVOC (Gainesville, FL, U.S.)* **2011**, 407–421; f) B. Zheng, H. Wang, Y. Han, C. Liu, Y. Peng, *Chem. Commun.* **2013**, *49*, 4561–4563.

[6] a) C. H. Heathcock, in: *Comprehensive Organic Synthesis* (Eds.: B. M. Trost, I. Fleming, C. H. Heathcock), Pergamon Elsevier, Oxford, UK, **1991**, vol. 2, p. 133; b) R. Ballini, R. Castagnani, M. Petrini, *J. Org. Chem.* **1992**, *57*, 2160–2162; c) J. M. Rodríguez, M. D. Pujol, *Tetrahedron Lett.* **2011**, *52*, 2629–2632.

[7] For the employment of MNO_2 as a nitrating reagent, see: a) A. Hassner, J. E. Kropp, G. J. Kent, *J. Org. Chem.* **1969**, *34*, 2628–2632; b) S. Ranganathan, S. K. Kar, *J. Org. Chem.* **1970**, *35*, 3962–3964; c) E. J. Corey, H. Estreicher, *J. Am. Chem. Soc.* **1978**, *100*, 6294–6295; d) J. Barluenga, M. A. Rodríguez, P. J. Campos, G. Asensio, *J. Chem. Soc., Chem. Commun.* **1987**, 1491–1492; e) J. Barluenga, M. A. Rodríguez, P. J. Campos, *J. Chem. Soc., Perkin Trans. 1* **1990**, 2807–2809; f) P. J. Campos, B. García, M. A. Rodríguez, *Tetrahedron* **2000**, *41*, 979–982; g) W. W. Sy, A. W. By, *Tetrahedron Lett.* **1985**, *26*, 1193–1196; h) S. S. Jew, H. D. Kim, Y. S. Cho, C. H. Cook, *Chem. Lett.* **1986**, 1747–1748; i) J. R. Hwu, K.-L. Chen, S. Ananthan, H. V. Patel, *Organometallics* **1996**, *15*, 499–505; j) D. Ghosh, D. E. Nichols, *Synthesis* **1996**, 195–197; for the employment of NO_2 as a nitrating reagent, see: k) H. Suzuki, T. Mori, *J. Org. Chem.* **1997**, *62*, 6498–6502; for the employment of NO as a nitrating reagent, see: l) T. Mukaiyama, E. Hata, T. Yamada, *Chem. Lett.* **1995**, 505–506; m) E. Hata, T. Yamada, T. Mukaiyama, *Bull. Chem. Soc. Jpn.* **1995**, *68*, 3629–3636; n) I. Jovel, S. Prateeptongkum, R. Jackstell, N. Vogl, C. Weckbecker, M. Beller, *Adv. Synth. Catal.* **2008**, *350*, 2493–2497; for the employment of a clay-supported nitrating reagent, see: o) R. S. Varma, K. P. Naicker, P. J. Liesent, *Tetrahedron Lett.* **1998**, *39*, 3977–3980.

[8] a) J. P. Das, P. Sinha, S. Roy, *Org. Lett.* **2002**, *4*, 3055–3058; b) A. Messere, A. Gentili, I. Garella, F. Temussi, B. D. Blasio, A. Fiorentino, *Synth. Commun.* **2004**, *34*, 3317–3324; c) A. S. Rao, P. V. Srinivas, K. S. Babu, J. M. Rao, *Tetrahedron Lett.* **2005**, *46*, 8141–8143; d) A. K. Bose, S. N. Ganguly, M. S. Manhas, W. He, J. Speck, *Tetrahedron Lett.* **2006**, *47*, 3213–3215; e) S. Ramgopal, K. Ramesh, A. Chakradhar, N. M. Reddy, K. C. Rajanna, *Tetrahedron Lett.* **2007**, *48*, 4043–4045; f) G. I. Nikishin, L. L. Sokova, V. D. Makhaev, N. I. Kapustina, *Russ. Chem. Bull.* **2008**, *57*, 118–123.

[9] For recent developments in the nitration of alkenes and decarboxylative nitration, see a) T. Taniguchi, T. Fujii, H. Ishibashi, *J. Org. Chem.* **2010**, *75*, 8126–8132; b) T. Taniguchi, T. Fujii, H. Ishibashi, *Org. Biomol. Chem.* **2011**, *9*, 653–655; c) P. K. Kancharla, Y. S. Reddy, S. Dharunam, Y. D. Vankar, *J. Org. Chem.* **2011**, *76*, 5832–5837; d) S. Maity, S. Manna, S. Rana, T. Naveen, A. Mallick, D. Maiti, *J. Am. Chem. Soc.* **2013**, *135*, 3355–3358; e) S. Maity, T. Naveen, U. Sharma, D. Maiti, *Org. Lett.* **2013**, *15*, 3384–3387; f) T. Naveen, S. Maity, U. Sharma,

D. Maiti, *J. Org. Chem.* **2013**, *78*, 5949–5954; g) B. V. Rokade, K. R. Prahhu, *Org. Biomol. Chem.* **2013**, *11*, 6173–6716; h) S. Manna, S. Jana, T. Saboo, A. Maji, D. Maiti, *Chem. Commun.* **2013**, *49*, 5286–5288; i) M. Al-Masum, N. Saleh, T. Islam, *Tetrahedron Lett.* **2013**, *54*, 1141–1144.

[10] a) M. C. Marcotullio, F. Epifano, M. Curini, *Trends Org. Chem.* **2003**, *10*, 21–34; b) K. Moriyama, M. Takemura, H. Togo, *Org. Lett.* **2012**, *14*, 2414–2417; c) B. Yu, A.-H. Liu, L.-N. He, B. Li, Z.-F. Diao, Y.-N. Li, *Green Chem.* **2012**, *14*, 957–962; d) H. Hussain, I. R. Green, I. Ahmed, *Chem. Rev.* **2013**, *113*, 3329–3371; e) A. Yoshimura, K. R. Middleton, A. D. Todora, B. J. Kastern, S. R. Koski, A. V. Maskaev, V. V. Zhdankin, *Org. Lett.* **2013**, *15*, 4010–4013; f) B. Poladura, A. Martinez-Castaneda, H. Rodriguez-Solla, R. Llavona, C. Concellon, V. del Amo, *Org. Lett.* **2013**, *15*, 2810–2813; g) F. Drouet, G. Masson, J. Zhu, *Org. Lett.* **2013**, *15*, 2854–2857.

[11] For a benzylic oxidation reaction, see: a) K. Moriyama, M. Takemura, H. Togo, *Org. Lett.* **2012**, *14*, 2414–2417; for the iodination of an aromatic ring, see: b) K. V. V. K. Mohan, N. Narender, S. J. Kulkarni, *Tetrahedron Lett.* **2004**, *45*, 8015–8018; for the nitration of a ring, see: c) M. A. Zolfigol, M. Bagherzadeh, E. Madrakian, E. Ghaemi, A. Taqian-Nasab, *J. Chem. Res., Synop.* **2001**, 140–142.

[12] 1-Nitro-2-phenylcyclohexene was reported to be obtained from the reaction of 1-phenylcyclohexene with $NaNO_2/I_2$/ethylene glycol in EtOAc/H_2O at 0 °C to room temperature for 72 h (see ref.[7h]). When we used the identical reaction conditions, styrene gave nitro alkene **2g** in 78% yield, whereas 1-phenylcyclohexene yielded 6-nitro-1-phenylcyclohexene (**2s**, by ^1H and ^{13}C NMR analyses of the crude reaction mixture).

[13] F. G. Bordwell, E. W. Garbisch Jr., *J. Org. Chem.* **1963**, *28*, 1765–1769.

[14] a) T. E. Stevens, W. D. Emmons, *J. Am. Chem. Soc.* **1958**, *80*, 338–341; b) M. S. Yusubov, I. A. Perederina, V. D. Filimonov, T.-H. Park, K.-W. Chi, *Synth. Commun.* **1998**, *28*, 833–836; c) E. N. Tveryakova, Y. Y. Miroshnichenko, I. A. Perederina, M. S. Yusubov, *Russ. J. Org. Chem.* **2007**, *43*, 152–153.

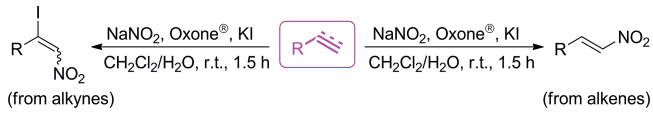
[15] Oxone® was reported to be capable of oxidizing the iodide ion to iodine/hypoiodide. For details, see: a) A. Yoshimura, C. Zhu, K. R. Middleton, A. D. Todora, B. J. Kastern, A. V. Maskaev, V. V. Zhdankin, *Chem. Commun.* **2013**, *49*, 4800–4802; b) M. C. Marcotullio, V. Campagna, S. Sternativo, F. Costantino, M. Curini, *Synthesis* **2006**, 2760–2766; c) M. Curini, F. Epifano, M. C. Marcotullio, F. Montanari, *Synlett* **2004**, 368–370.

[16] C. Bolm, A. S. Magnus, J. P. Hildebrand, *Org. Lett.* **2000**, *2*, 1172–1175.

[17] a) J. Park, C. Song, K. Choi, T. Sim, B. Moon, E. J. Roh, *Bioorg. Med. Chem. Lett.* **2013**, *23*, 5515–5518; b) S. Jalal, S. Sarkar, K. Bera, S. Maiti, U. Jana, *Eur. J. Org. Chem.* **2013**, 4823–4828; c) J. Liu, X.-R. Zhu, J. Ren, W.-D. Chen, B.-B. Zeng, *Synlett* **2013**, *24*, 2740–2742; d) L. Rokhom, G. Bez, *Tetrahedron Lett.* **2013**, *54*, 5500–5504; e) A. G. Myer, J. K. Barbay, B. Zhong, *J. Am. Chem. Soc.* **2001**, *123*, 7207–7219; f) O. A. Ivanova, E. B. Averina, E. M. Budynina, A. A. Korlyukov, M. Y. Antipin, T. S. Kuznetsova, T. S. Zefirov, *Russ. J. Org. Chem.* **2005**, *41*, 1292–1297.

Received: June 13, 2014
Published Online: ■

EurJOC European Journal of Organic Chemistry



(from alkynes) (from alkenes)

Oxone® ($2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$) was used to promote the reactions of alkenes and alkynes with sodium nitrite ($NaNO_2$) and potassium iodide (KI) to afford the corresponding nitro and β-iodonitro-substituted alkenes, respectively, in moderate to good yields.

S. Hlekhlai, N. Samakkanad, T. Sawangphon, M. Pohmakotr, V. Reutrakul, D. Soorukram, T. Jaipetch, C. Kuhakarn* 1–11

Oxone®/KI-Mediated Nitration of Alkenes and Alkynes: Synthesis of Nitro- and β-Iodonitro-Substituted Alkenes

Keywords: Synthetic methods / Green chemistry / Alkenes / Alkynes / Oxidation / Nitration

