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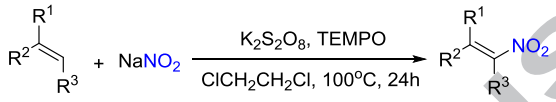

transition-metal-free
28 examples
up to 96% yield
highly *E*-selectivity

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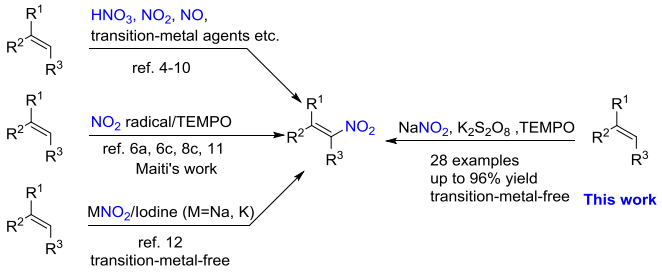
ABSTRACT

A transition-metal-free nitration of alkenes with $NaNO_2$ in the presence of $K_2S_2O_8$ and 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) is developed. The transformation exhibits a broad substrate scope and good functional group tolerance, thus providing a new and expedient protocol for stereoselective synthesis of (*E*)-nitroalkenes with moderate to good yields. Moreover, the nitration processes of (*E*)- and (*Z*)-stilbene are also studied: even though the proportion of substrates is different, the *E/Z* ratio of the products is basically the same. Based upon experimental observations, a possible reaction mechanism is proposed.

Direct nitration of alkenes has attracted much attention because the resulting nitroalkenes are vital important intermediates in natural pharmaceuticals and chemical industry.[1] Besides, nitroalkenes can be easily used in various organic transformations, including the construction of different carbon skeletons,[2] and the formation of amines, heterocyclics, hydroxylamines, oximes and nitroso compounds.[3] Consequently, considerable efforts have been made for the development of direct nitration of alkenes (Scheme 1). In previous studies, direct alkene nitration involved HNO_3[4] and nitrogen oxides[5] like NO and NO_2 as the nitro agents. However, these strategies suffer from harsh reaction conditions, narrow substrate scope and poor functional group tolerance. Alternatively, transition-metal agents such as $AgNO_2$,[6] $AgNO_3$,[7] $Fe(NO_3)_3$,[8] and $Cu(NO_3)_2$[9] have also been employed in the nitration process.[6-10] Among them, Maiti and coworkers reported the direct nitration process with nitrite or nitrate/2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO),[6a, 6c, 8c, 11] and these protocols have made great significants in this field. Recently, Nichols and Kuhakarn independently reported the transition-metal-free nitrification of styrene with alkaline metals MNO_2 (M=K, Na) in the presence of stoichiometric amount of iodine.[12] Unfortunately, these nitration approaches have some limitations including poor substrate scope and poor functional group tolerance. Despite these advances, it is still highly desirable to develop novel approaches for the construction of nitroalkene compounds. According to Yang's work, when *N*-methyl-*N*-arylacrylamide reacted with $NaNO_2$ and $K_2S_2O_8$, only nitro-containing oxindoles were obtained.[13] Herein we report a transition-metal-free nitration of alkenes with $NaNO_2$ that combined $K_2S_2O_8$ and TEMPO in this system. The present method is characterized by its broad substrate scope and high functional group compatibility utilizing inexpensive and easily accessible reagents, thus offering a simple and efficient approach for stereoselective construction of (*E*)-nitroalkenes. Moreover, the stereoselectivities of nitration were also discussed with different proportion of (*E*)- and (*Z*)-stilbene, nitro products with almost the same *E/Z* ratio were obtained.



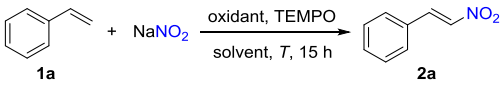
Scheme 1. Different methods to synthesize nitroalkenes

The reaction of styrene with $NaNO_2$ in the presence of $K_2S_2O_8$ and TEMPO at 100 °C for 24 h in 1,2-dichloroethane ($ClCH_2CH_2Cl$) gave *β*-nitrostyrene in 85% isolated yield. Hydrogen atom at the *β*-position of styrene was substituted by a NO_2 group, and only (*E*)-*β*-nitrostyrene was obtained.

The initial survey of the reaction conditions was performed with styrene as the model substrate, and the results were summarized in Table 1. $K_2S_2O_8$ and TEMPO were crucial for the nitration. In the absence of $K_2S_2O_8$ or TEMPO, *β*-nitrostyrene were not obtained (Table 1, Entries **1**-**2**). Changing the solvent to CH_3CN or DMSO afforded only 33-36% yield of desired product (Table 1, Entries **3**-**5**). Among the reaction temperature screened, 100 °C was found to be the most effective (Table 1, Entries **3**, **6**-**7**). Subsequently, increasing the amount of $K_2S_2O_8$ resulted in a slight drop in terms of product yield (Table 1, Entries **3**, **8**-**9**).

Increasing the amount of TEMPO increased the yield of **2a** (Table 1, Entries **8** and **10**), while a comparable yield (70%) was obtained when the amount of TEMPO was increased to 1.5 equiv. (Table 1, Entry **11**). The influence of $NaNO_2$ loading was also investigated, a higher yield was obtained when the amount of $NaNO_2$ was 1.5 equiv. (Table 1, Entries **8**, **12**-**13**). Oxidant screening indicated that $K_2S_2O_8$ was the best choice for this reaction (Table 1, Entries **12**, **14**-**15**). To our delight, a longer reaction time improved the yield (Table 1, Entry **16**). In all cases, (*E*)-nitro alkene was obtained as a single stereoisomer.

Table 1. Screening of the reaction conditions.[a]



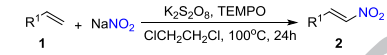
1a **2a**

Entry	$NaNO_2$ (equiv.)	Oxidant (equiv.)	TEMPO (equiv.)	solvent	*T* (°C)	Yield[b] (%)
1	2.0	$K_2S_2O_8$ (2.5)	-	$ClCH_2CH_2Cl$	100	trace
2	2.0	-	1.2	$ClCH_2CH_2Cl$	100	0
3	2.0	$K_2S_2O_8$ (2.5)	1.2	$ClCH_2CH_2Cl$	100	68
4	2.0	$K_2S_2O_8$ (2.5)	1.2	CH_3CN	100	36
5	2.0	$K_2S_2O_8$ (2.5)	1.2	DMSO	100	33
6	2.0	$K_2S_2O_8$ (2.5)	1.2	$ClCH_2CH_2Cl$	80	61
7	2.0	$K_2S_2O_8$ (2.5)	1.2	$ClCH_2CH_2Cl$	120	58
8	2.0	$K_2S_2O_8$ (2.0)	1.2	$ClCH_2CH_2Cl$	100	71
9	2.0	$K_2S_2O_8$ (3.0)	1.2	$ClCH_2CH_2Cl$	100	61
10	2.0	$K_2S_2O_8$ (2.0)	0.5	$ClCH_2CH_2Cl$	100	67
11	2.0	$K_2S_2O_8$ (2.0)	1.5	$ClCH_2CH_2Cl$	100	70
12	1.5	$K_2S_2O_8$ (2.0)	1.2	$ClCH_2CH_2Cl$	100	74
13	2.5	$K_2S_2O_8$ (2.0)	1.2	$ClCH_2CH_2Cl$	100	58
14	1.5	$Na_2S_2O_8$ (2.0)	1.2	$ClCH_2CH_2Cl$	100	67
15	1.5	$(NH_4)_2S_2O_8$ (2.0)	1.2	$ClCH_2CH_2Cl$	100	51
16[c]	1.5	$K_2S_2O_8$ (2.0)	1.2	$ClCH_2CH_2Cl$	100	92

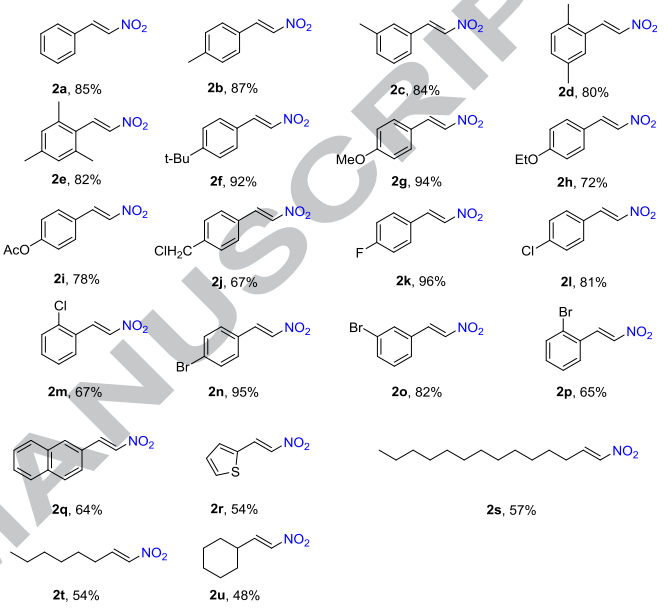
[a] Reaction conditions: styrene (0.5mmol), $NaNO_2$, oxidant, TEMPO, solvent (2 mL), *T*, 15 h. [b] Determined by GC. [c] Reaction time: 24 h.

With the optimized reaction conditions in hand, the substrate scope of the reaction was explored. First, mono substituted alkenes were studied, and the results are summarized in Table 2. All the products were (*E*) stereoisomer only in contrast to the earlier-reported methods.[5a] Styrene was smoothly nitrated to provide product **2a** in 85% isolated yield. Diverse functionality like alkyl, alkoxy, acetoxy and chloromethyl were well tolerated (Table 2. **2b**-**2j**). Compared with the previous transition-metal-free methods,[12] this transformation exhibits better generality. For example, styrenes containing electron-donating substituents like 4-Me and 4-OMe could also provide corresponding nitro products (Table 2. **2b**, **2g**). Notably, nitroalkenes with steric hindrance were still achieved in good yield (Table 2. **2d**-**2e**). The reaction was found to be compatible with fluorine, bromine, and chlorine groups on the aryl ring (Table 2. **2k**-**2p**), and the corresponding products are useful for further functionalization. Styrenes containing the same substituent at different positions of the aryl ring had an influence on the efficiency of this nitration. For example, 4-bromo-styrene gave higher yield than 3-/2-bromo-styrene (Table 2, **2n**-**2p**). 2-Vinyl naphthalene was also obtained in good yield (Table 2. **2q**). A heterocyclic alkene, 2-vinyl thiophene, underwent the reaction to provide the desired product in 54% yield (Table 2. **2r**). While the aliphatic nitroalkenes, like (*E*)-1-nitro-1-tetradecene, (*E*)-1-nitro-1-octene and (*E*)-(2-nitrovinyl)cyclohexane were also obtained in 48-57% yield (Table 2. **2s**-**2u**). In summary, nitroalkenes were obtained in good yield ranging from 48-96% (Table 2. **2a**-**2u**).

Table 2. Nitration reaction of mono substituted alkenes.[a]



1 **2**

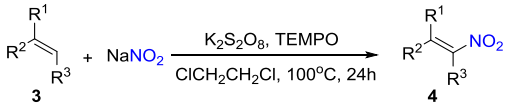


[a] Reaction condition: Alkenes (0.5mmol), $NaNO_2$ (1.5 equiv.), $K_2S_2O_8$ (2.0 equiv.), TEMPO (1.2 equiv.), $ClCH_2CH_2Cl$ (2 mL), 100 °C, 24 h. Isolated yields.

To investigate the stereo-selectivity of nitration, multi substituted alkenes were examined. As expected, the corresponding nitro products were achieved smoothly under the optimized reaction condition (Table 3). When Me was installed at *α*- or *β*-position of styrene, a > 6:1 *E*/*Z* mixture was obtained for nitroalkenes (Table 3. Entries **1**, **3**). 1,1-diphenylethylene underwent the nitration to form the desired product in 88% yield (Table 3. Entry **2**). When stilbene was chosen as the substrate, the yield of nitroalkenes decreased significantly, and the *E*/*Z* ratio was almost the same (Table 3. Entries **4**-**5**). It is worth noting that 3-nitro-1,2-dihydronaphthalene and 1-nitrocyclohexene were achieved under the optimized reaction condition (Table 3. Entries **6**-**7**). Additional, chalcone and norbornylene did not provide the desired product in this transformation (Table 3. Entries **8**-**9**).

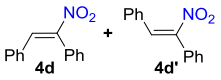
Based on the results outlined in Table 2 and 3, it's interesting that the mono substituted alkenes, disubstituted alkenes that R^1=R^2 and cyclic alkenes, could undergo the reaction to obtain (*E*) stereoisomer of nitroalkenes only (Table 2 and Table 3, Entries **2**, **6**-**7**). On the other hand, multi substituted alkenes with the group $R^1 \neq R^2$ except cyclic alkenes could be converted to the mixtures of (*E*) and (*Z*) stereoisomer of corresponding nitroalkenes, and the (*E*) stereoisomer was the main product (Table 3, Entries **1**, **3**-**5**).

Table 3. Nitration reaction of multi substituted alkenes.[a]



3 **4**

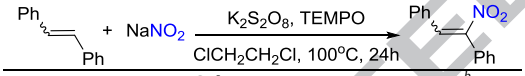
Entry	R^1	R^2	R^3	Product **4**	Yield of **4**

1	Me	Ph	H	**4a**	62%[b](*E*:*Z*=6:1)[c]
2	Ph	Ph	H	**4b**	88%
3	H	Ph	Me	**4c**	78%[b](*E*:*Z*=8:1)[c]
4[d]	H	Ph	Ph	 **4d** + **4d'**	35%[b](*E*:*Z*=2.4:1)[c]
5[d]	Ph	H	Ph		39%[b](*E*:*Z*=2.3:1)[c]
6				**4e**	81%
7				**4f**	62%
8	Ph	H	Bz	**4g**	N.D.
9				**4h**	N.D.

[a] Reaction condition: Alkenes (0.5mmol), $NaNO_2$ (1.5 equiv.), $K_2S_2O_8$ (2.0 equiv.), TEMPO (1.2 equiv.), $ClCH_2CH_2Cl$ (2 mL), 100 °C, 24 h. Isolated yields. [b] Yield of (*E*) stereoisomer only. [c] Determined by ^1H NMR. [d] The product was mainly (*E*)-(1-nitroethene-1,2-diyl)dibenzene.

Next, stilbene was chosen to study the stereoselectivity of this method (Table 4). Under the optimized reaction conditions, the (*E*) nitro compound was achieved as the main product. It is noteworthy that regardless the ratio of (*E*)- and (*Z*)-stilbene, the *E*/*Z* ratio of the products was ~2.3-2.7:1 determined by ^{1}HNMR (Table 4, Entries **1**-**5**). Interestingly, when (*Z*)-stilbene was chosen as the substrate, (*E*)-stilbene was detected by TLC at the end of reaction. The reason for this phenomenon may be the different thermodynamic stabilities between (*E*)- and (*Z*)-stilbene. Under the optimized condition (100 °C), (*Z*)-stilbene could be transformed into (*E*)-stilbene in the reaction process (see below).

Table 4. Stereoselective nitration reaction.[a]

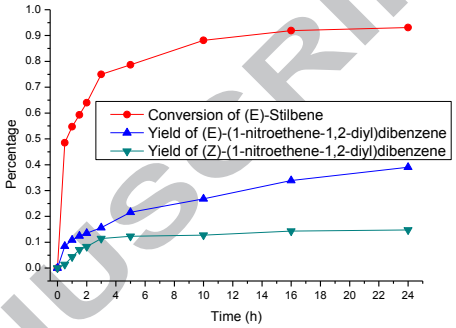


Entry	Substrate	*E*:*Z*[b]
1	(*E*)-stilbene	2.30:1
2	(*Z*)-stilbene	2.43:1
3	(*E*)- and (*Z*)-stilbene (1:1)	2.68:1
4	(*E*)- and (*Z*)-stilbene (2:1)	2.36:1
5	(*E*)- and (*Z*)-stilbene (1:2)	2.51:1

[a] Reaction condition: Stilbene (0.5mmol), $NaNO_2$ (1.5 equiv.), $K_2S_2O_8$ (2.0 equiv.), TEMPO (1.2 equiv.), $ClCH_2CH_2Cl$ (2 mL), 100 °C, 24 h. [b] Determined by ^1H NMR.

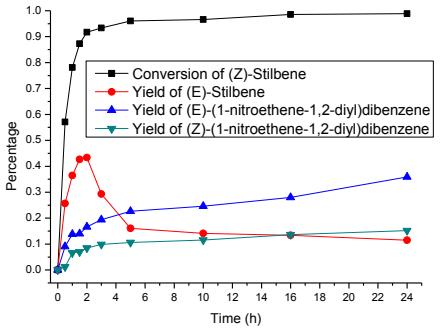
In order to verify the inference, the process of the nitration under standard condition was investigated. The nitration of (*E*)- and (*Z*)-stilbene monitored by GC-MS are shown in Figure 1 and 2, respectively. As shown in Figure 1, with increasing reaction time, the conversion of (*E*)-stilbene increased fast at first and then slowed down. The yield of (*E*)-(1-nitroethene-1,2-diyl)dibenzene increased faster than that of (*Z*) nitro product. In this process, when the substrate was (*E*)-stilbene, (*E*)-(1-nitroethene-1,2-diyl)dibenzene was the main product, and the *E*/*Z* ratio of nitro products was about 2.42:1. It is clearly that no (*Z*)-stilbene was found in reaction process. In another case, from Figure 2, with the time going by, the conversion of (*Z*)-stilbene increased fast from 0 to 2 h, and then came to a balance. The increasing tendency of (*E*) and (*Z*) nitro products was similar to Figure 1. It could be found that (*E*)-stilbene was detected in the whole process, which was consistent with the result detected by TLC. The yield of (*E*)-stilbene increased firstly and then decreased to 11%. Notably, the (*E*) nitro product was also the main product in this process, the *E*/*Z* of products calculated about 2.36:1. From these two figures, it's shown that (*Z*)-stilbene was converted into (*E*)-stilbene at first when it was chosen as the substrate, and then the (*E*) compound underwent the reaction to obtain the corresponding products. This could explain the results in Table 4, that the *E*/*Z* ratio of nitro products was approximately equal, even the initial loading of (*E*)- and (*Z*)-stilbene was different.

Figure 1. The nitration process of (*E*)-stilbene.[a]



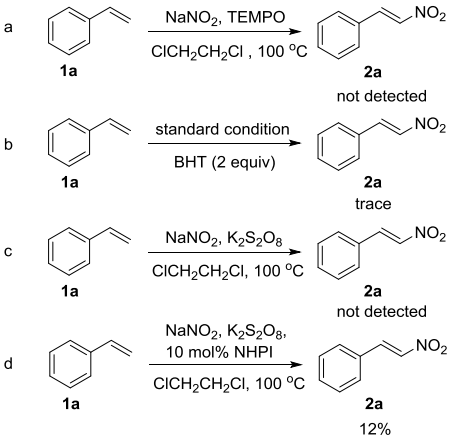
[a] Reaction condition: (*E*)-stilbene (0.5mmol), $NaNO_2$ (1.5 equiv.), $K_2S_2O_8$ (2.0 equiv.), TEMPO (1.2 equiv.), $ClCH_2CH_2Cl$ (2 mL), 100 °C. Detected by GC-MS.

Figure 2. The nitration process of (*Z*)-stilbene.[a]



[a] Reaction condition: (*Z*)-stilbene (0.5mmol), $NaNO_2$ (1.5 equiv.), $K_2S_2O_8$ (2.0 equiv.), TEMPO (1.2 equiv.), $ClCH_2CH_2Cl$ (2 mL), 100 °C. Detected by GC-MS.

Several control experiments were carried out to probe the mechanism of this nitration method. According to the literature,[13]

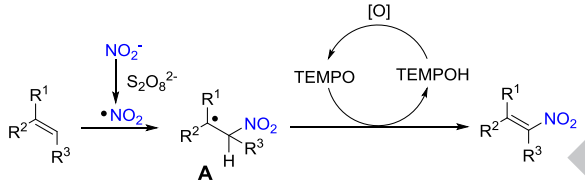


Standaed conditions: styrene (0.5mmol), $NaNO_2$ (1.5 equiv.), $K_2S_2O_8$ (2.0 equiv.), TEMPO (1.2 equiv.), $ClCH_2CH_2Cl$ (2 mL), 100 °C, 24 h. For a, without $K_2S_2O_8$ (2.0 equiv.). For b, BHT (2.0 equiv.) was added. For c, without TEMPO (1.2 equiv.). For d, TEMPO (1.2 equiv.) was replaced by NHPI (10 mol%). Detected by GC/GC-MS.

Scheme 2. Control experiments.

NO_2^- could form a nitrogen dioxide radical in the presence of $K_2S_2O_8$. Without addition of $K_2S_2O_8$, (*E*)-*β*-nitrostryene was almost not detected by GC and GC-MS (Scheme 2a). When the radical inhibitor, 2,6-*di*-*tert*-butyl-4-methylphenol (BHT) was added in the standard reaction, trace product was detected (Scheme 2b). This result indicated that the reaction presumably underwent a radical pathway. And another control experiment showed that the nitro product was not obtained without TEMPO (Scheme 2c). For further research the role of TEMPO, *N*-hydroxyphthalimide (NHPI) was added into this reaction to replace TEMPO, and (*E*)-*β*-nitrostryene was obtained in 12% yield (Scheme 2d). It indicated that TEMPO could abstract the hydrogen atom like phthalimide-*N*-oxyl radical (PINO) which could be generated from NHPI under oxidation condition[14]. And the intermediate TEMPOH was also detected by GC-MS[15].

Based on the above experimental results and previous reports[6c, 8c, 9, 11, 13, 16], a plausible mechanism is proposed and shown in Scheme 3. Firstly, NO_2^- reacted with $S_2O_8^{2-}$ to generate a nitrogen dioxide radical, and then the free radical added to the carbon–carbon double bond of alkene to afford the intermediate **A**. TEMPO abstracted the hydrogen atom next to nitro group, and the carbon–carbon double bond was formed. Though the plausible mechanism is supported, more details still need to be studied.



Scheme 3. Proposed mechanism of nitration method.

In summary, an efficient transition-metal-free, $K_2S_2O_8$-mediated direct nitration of alkenes with $NaNO_2$ in the presence of TEMPO was developed. A wide range of alkenes including styrenes, heterocyclic and aliphatic alkenes were compatible under this condition, affording (*E*)-nitroalkenes in moderate to good yields. Moreover, the effect of the stereostructures of alkene on the stereoselectivity of nitro products were also studied: even though the proportion of (*E*)- and (*Z*)- substrates is different, the *E/Z* ratio of the resulting nitro products is almost the same.

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