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Radical Enamination of Vinyl Azides: Direct Synthesis of *N*-Unprotected Enamines

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Supporting Information

ABSTRACT: An electron-withdrawing-group-generable radical-induced enamination of vinyl azides is reported, which results in a variety of β-functionalized *N*-unprotected enamines in a stereoselective manner. A plausible mechanism involving an unusual 1,3-H transfer of in situ generated iminyl radical intermediate was proposed on the basis of experimental results and DFT calculations.

Vinyl azides are a class of structurally unique and synthetically useful functionalized alkenes,[1] which were first reported as early as 1910.[2] In the past decade, the renaissance of vinyl azide chemistry has been witnessed, as proven by the enormous novel transformations reported in the literature,[3] which may be owing to the great impetus given by transition-metal catalysis[4] as well as the latest development of practical preparation protocols.[5] The numerous transformations of vinyl azides provide reliable synthetic approaches to diverse, structurally distinct molecular frameworks, typically including hetero/carbocycles,[6] amides,[7] ketones,[8] and 2*H*-azirines,[9] etc. In the present work, we focus on establishing the relationship between vinyl azides and enamines. *N*-Unprotected enamines are synthetically very useful, with applications in the synthesis of heterocycles,[10] chiral amines,[11] and as drug structures in their own right.[12] However, the synthetic methods have been less developed, and moreover, the available protocols usually suffer from disadvantages such as limited substrate scope, tedious multistep operation, and/or harsh conditions.[13] Consequently, a practical and efficient synthetic method for *N*-unprotected enamines is in high demand. Structurally, vinyl azides can be classified as *N*-diazoenamines, and therefore extrusion of nitrogen molecule should be a rather straightforward way to synthesize *N*-unprotected enamines. However, such a methodology has not yet been established so far, probably due to the sensitivity to hydrolysis. We envisage an electron-withdrawing group (EWG)-generable radical-induced enamination of vinyl azides could be feasible, in which an EWG is introduced onto the terminal of vinyl azides by radical addition and then stabilize the enamine product (Figure 1a).[6,8,14] We eventually realize this goal using nitro, acyl, and sulfonyl radicals,[15] thereby providing a general approach to access a variety of β-functionalized *N*-unprotected enamines (Figure 1b). To our knowledge, this is the first example of the conversion of vinyl azides into enamines.[1,3]

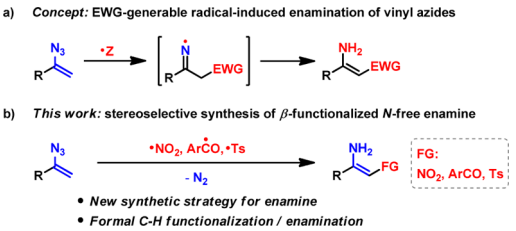

Figure 1. Strategies for converting vinyl azides into β-functionalized *N*-unprotected enamines.

Considering the strong electron-withdrawing property of the nitro group,[16] the study was initialized with nitrification reaction. After several trials, the optimal conditions were identified as follows: α-tolyl vinyl azide **1a** (0.5 mmol), $AgNO_2$ (1.0 mmol), H_2O (1.0 mmol), in 1,4-dioxane at 60 °C, with 81% yield of (Z)-2-nitroenamine **2aa**. Around the optimal conditions, the reaction parameters were varied and some results are summarized in Table 1. Except for $AgNO_2$,[17] other nitro sources that have been employed in nitrification reaction, including $NaNO_2$, $AgNO_3$, $Fe(NO_3)_3{\cdot}9H_2O$, $Cu(NO_3)_2{\cdot}3H_2O$, $Bi(NO_3)_3{\cdot}3H_2O$ and *tert*-butyl nitrite,[18] were found to be either totally ineffective or produced the hydrolyzed product **2aa′** (entries 1−7). Furthermore, the necessity of H_2O was confirmed in a control experiment (entry 8).

With the optimal conditions in hand, we set out to study the scope of vinyl azides in nitrification. As shown in Scheme 1, the substrate scope is quite broad, as a wide range of aryl, heteroaryl, alkyl, and alkenyl vinyl azides were all suitable in this transformation, thereby affording the desired β-nitroenamines in high efficiency. For instance, the vinyl azides **1ab**−**1ao** with aromatic substituents, including aryl, fused aryl, and heteroaryl

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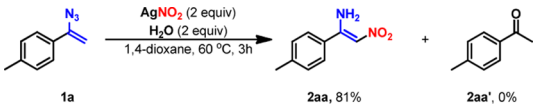
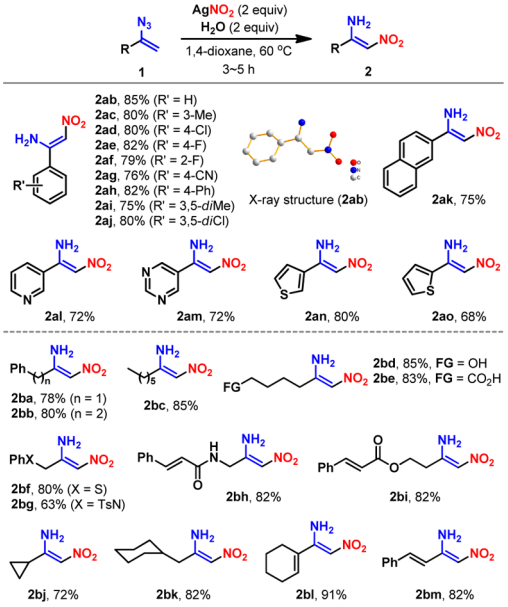
Table 1. Optimization of the Reaction Conditions[a]



entry	variation from standard conditions	yield of **2aa** (%)	yield of **2aa′** (%)
1	$NaNO_2$, instead of $AgNO_2$	0	0
2	$AgNO_3$, instead of $AgNO_2$	trace	30
3	$Pb(NO_3)_2$, instead of $AgNO_2$	0	60
4[b]	$Fe(NO_3)_3{\cdot}9H_2O$, instead of $AgNO_2$	0	82
5[b]	$Cu(NO_3)_2{\cdot}3H_2O$, instead of $AgNO_2$	0	40
6[b]	$Bi(NO_3)_3{\cdot}3H_2O$, instead of $AgNO_2$	0	75
7	*tert*-Butyl nitrite, instead of $AgNO_2$	0	0
8	without H_2O	0	trace

[a]Isolated product yield. [b]Without additional 2 equiv of H_2O.

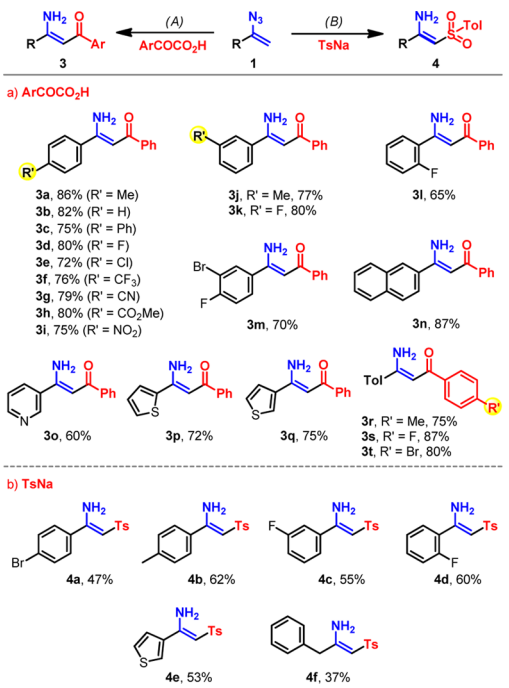
Scheme 1. Conversion of Vinyl Azides into β-Nitroenamines



groups, underwent smooth reaction with $AgNO_2$ to give the products **2ab**–**2ao** in 68–85% yields. Pleasingly, the steric and electronic factors of aryl groups did not show significant influence on reaction efficacy. The (Z)-configuration of the alkene was unambiguously confirmed by X-ray diffraction analysis of **2ab**. Note that heteroaromatic substituents such as pyridyl, pyrimidinyl, and thienyl could be smoothly incorporated onto the nitroenamine products **2al**–**2ao** by choosing the corresponding vinyl azide reactant. Similarly, application of this reaction to α-alkyl vinyl azides revealed high reaction efficiency and excellent functional group tolerance. For example, simple α-alkyl-vinyl azides resulted in the desired products **2ba**–**2bc** in high yields. Moreover, the functionality such as hydroxyl, carboxyl, thioether, amide, and ester at the terminal of alkyl group was well tolerant, thereby affording the functionalized β-nitroenamines **2bd**–**2bi** in 63–85% yields. Moreover, the alicyclic such as cyclopropyl and cyclohexyl groups was also compatible and led to the desired products **2bj** and **2bk** in 72% and 82% yields. Further, the alkenyl substituents such as cyclohexenyl and styryl were tolerant, with the generation of α-alkenyl-β-nitroenamines **2bl** and **2bm** in 91% and 82% yields.

Following this success with formal C–H nitrification/enamination of vinyl azides, we turned our attention to the reactivity of EWG-generable radicals beyond nitro radical. First, we examined the reactivity of benzoyl radical which could be generated from the decarboxylation of α-ketonic acids.[19] Initially, with silver catalysis we were able to isolate an enaminone product **3a** in the reaction of **1a** with benzoylformic acid, but the yield was very low. Fortunately, use of CuI as the catalyst was capable of efficiently catalyzing the conversion of vinyl azides into enaminones (Scheme 2). The reaction scope was broad, as a

Scheme 2. Variation of Radicals[a]



[a]Reaction conditions (A): **1** (0.50 mmol), $ArCOCO_2H$ (0.6 mmol), H_2O (1.0 mmol), CH_3CN (2 mL), CuI (10 mol %) at 70 °C for 4–5 h under air. Reaction conditions (B): **1** (0.50 mmol), TsNa (1.0 mmol), H_2O (1.0 mmol), $AgNO_3$ (20 mol %), NMP (2 mL), at 60 °C for 24 h under O_2. Isolated product yields.

variety of vinyl azides could be applied in the reaction with α-ketonic acids to give products **3a**–**3t** stereoselectively in 60–87% yields. Further, this C–H functionalization/enamination strategy of vinyl azides was successfully extended to sulfonyl radical, which allowed for the synthesis of β-sulfonyl enamines **4a**–**4f** in good product yields and also in a stereoselective manner.[20] As a result, a general transformation of vinyl azides into diverse β-functionalized *N*-unprotected enamines was established. The stereochemistry may stem from the intramolecular hydrogen bonding effect between the amino group and the oxygen of the electron-deficient functions. Note that the majority of these *N*-unprotected enamines in Schemes 1 and 2 are novel compounds which could prove useful as intermediates in organic and medicinal chemistry research.

To evaluate the scalability of the methodology, we further transformed the β-functionalized primary enamines to many bioactive molecules as useful building blocks according to the literatures (Scheme 3). For example, hydrolysis of the resulting β-functionalized primary enamines with dilute sulfuric acid could furnish ketones in high yields (**5b**, **5h**). Furthermore, 2*H*-azirine **5a** was obtained in middle yield with PhIO in trifluoroethanol.[21]

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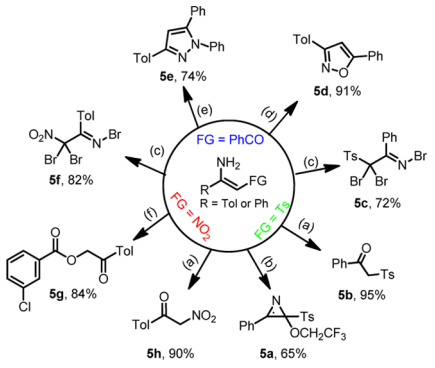
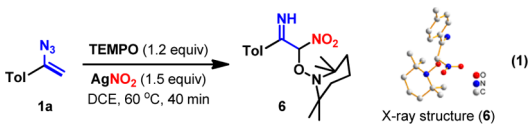
Scheme 3. Further Transformations of β-Functionalized Enamines[a,b]



[a]Reaction conditions: (a) stir in CH_2Cl_2 with dilute sulfuric acid at room temperature for 3 h; (b) PhIO (2.0 mmol) in TFE (5 mL) stirred at room temperature for 15 min, then substrate (1 mmol in 5 mL of TFE) was added dropwise; (c) substrate (0.5 mmol), NBS (1.65 mmol), DCE (3 mL), at rt for 12 h; (d) substrate (0.5 mmol), $NH_2OH{\cdot}HCl$ (1.0 mmol) in CH_3CN at 100 °C; (e) substrate (0.5 mmol), $PhNHNH_2$ (1.0 mmol) in CH_3CN at 100 °C; (f) substrate (0.5 mmol), *m*-CPBA (1.0 mmol) in CH_2Cl_2 for 12 h. [b]Isolated yields.

Morever, polybrominated imines **5c** and **5f** were also synthesized by treating with NBS,[22] and the structure of **5f** was confirmed by crystallography analysis (see the Supporting Information), α-ester ketone **5g** was directly prepared by the treatment with *m*-CPBA. Finally, β-acyl primary enamines with hydroxylamine hydrochloride and phenylhydrazine hydrate gave the isoxazole (**5d**) and pyrrole products (**5e**) in high yield.[23]

To gain insight into the reaction mechanism, TEMPO, a radical scavenger,[24] was added into the reaction of vinyl azide **1a** with $AgNO_2$; unexpectedly, a TEMPO-coupled compound **6** was isolated as the sole product,[25] with the structure confirmation by X-ray diffraction analysis (eq 1). This result clearly demonstrated

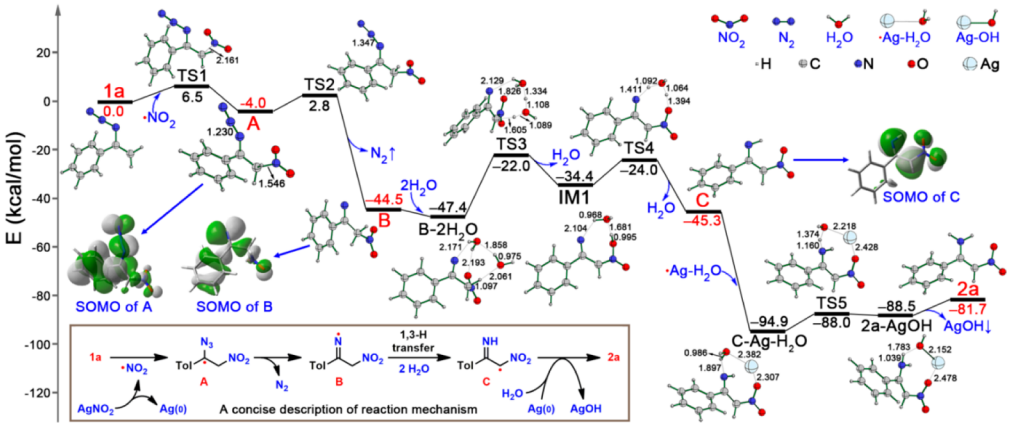


α-imine radical intermediate was involved in the reaction process, and its generation probably proceeds by an unusual 1,3-H transfer from iminyl radical,[26] by comparison with precedent radical reactions of vinyl azides.[14]

On the basis of above experimental result and related precedents,[6,8,14] a plausible reaction mechanism was proposed and rationalized by DFT calculations at M06/6-311++G(d,p) (SDD for Ag) level. As depicted in Scheme 4, following the decomposition of $AgNO_2$ to release nitro radical ($\cdot NO_2$) and Ag(0),[17] the attack of $\cdot NO_2$ radical to the terminal carbon of vinyl azide **1a** occurs, leading to intermediate A. The energy barrier (E_b) and reaction energy (RE) for such attack are 6.5 (TS1) and −4.0 (**A**) kcal/mol, respectively. The singly occupied molecular orbital (SOMO, i.e., the radical orbital) of **A** is a π orbital, which delocalizes on whole molecule with non-ignorable distribution on azido group and may influence its N−N bonding. Subsequently, the iminyl radical **B** is formed by releasing N_2 from **A**, with a low E_b of 6.8 kcal/mol (TS2) and a large RE of −40.5 kcal/mol. The SOMO of **B** is a σ orbital and distributes largely on iminyl N atom, which may be responsible for the experimentally verified unusual 1,3-H transfer. Such a transfer is generally considered as an unfavorable process, so we designed three possible pathways for explaining the transfer mechanism, including the direct transfer and one or two H_2O-aided transfer.[27] We are pleased to find such a transfer process is possible with two H_2O assistance by two steps: first, H atom is transferred to the *O*-atom of nitro group (**B**−2H_2O → TS3 → IM1) with E_b of 25.4 kcal/mol, and further transferred to iminyl *N*-center (IM1 → TS4 → **C**) with E_b of 10.4 kcal/mol. The SOMO of **C** is a π orbital and mainly distributed on β-C and imine *N*-atoms. Therefore, both β-C and imine N can be the valid sites for eliminating the radical. According to our calculations, TEMPO captures the C through β-C-site because the formation of product **6** (eq 1) is thermodynamically favorable (exergonic by −20.2 kcal/mol). In contrast, if TEMPO captures C through imine *N*-site, the formation of coupling product is slightly endergonic (0.5 kcal/mol).[28] Even though **C** is only 0.8 kcal/mol lower in energy than B, it can bind hydrate of elemental silver (Ag(0)-H_2O), which not only eliminates the radical on C, but also releases energy by 49.6 kcal/mol. Such a large binding energy will strongly promote the reaction forward. The resulted **C**−Ag−H_2O complex can be easily converted to **2a** by the transfer of an H atom from water to iminyl *N*-site through TS5 (E_b = 6.9 kcal/mol) and the formation of AgOH precipitation. Obviously, H_2O acts as H-shuttle and plays a crucial role in the reaction.

In summary, the first synthetically useful conversion of vinyl azides into enamines is reported by an electron-withdrawing

Scheme 4. Proposed Mechanism



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group-stabilizing strategy. A variety of β-functionalized *N*-unprotected enamines, including β-nitro, acyl, and sulfonyl, can be prepared by this approach in a stereoselective manner, thus providing a general route to access this kind of functionalized alkenes. An unusual 1,3-H transfer was disclosed on the basis of experimental results and DFT calculations. This strategy represents an appealing means to achieve *N*-unprotected enamine synthesis; extension to other radical species is under way, and will be reported in due course.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.7b03204.

Experimental procedures and spectra copies (PDF)

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Notes

The authors declare no competing financial interest.

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