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Ambient Benzotriazole Ring Opening through Intermolecular Radical Addition to Vinyltriazole

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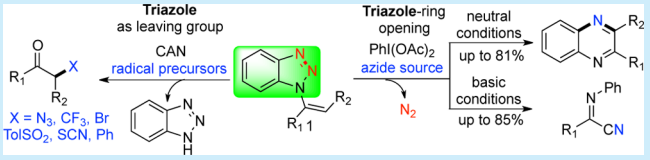
Supporting Information

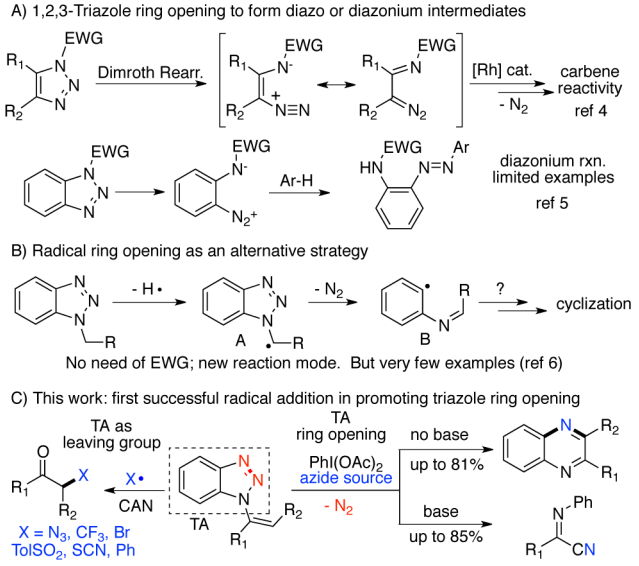
ABSTRACT: Radical addition to vinyltriazole was developed as a new approach to achieve 1,2,3-triazole ring opening under mild conditions. Through reagent control, excellent chemoselectivity was achieved, giving either nitrile under basic conditions or quinoxaline under neutral conditions. Reactivities made this method an attractive new reaction mode.



Discovery of copper- and ruthenium-catalyzed azide−alkyne cycloaddition[1] has made 1,2,3-triazole (TA) one of the most important heterocycles in chemical, material, and biological research during the past decade.[2] Recently, studies regarding the chemical and physical properties of this heterocycle have gained more attention because of progress in using TA as a ligand or as a building block in complex molecule synthesis. One particularly interesting area is the "ring opening" through extrusion of nitrogen gas for the preparation of complex N-heterocyclic compounds.

As shown in Scheme 1A, it is known that electron-withdrawing group activated TA can undergo Dimroth rearrangement[3] to give the ring-opening diazoimine intermediate. On the basis of this unique reactivity, Fokin and others developed a series of new transformations through dirhodium-catalyzed diazo activation.[4] Those studies are highly attractive because triazole compounds can act as an alternative source of "diazo" synthon. Benzotriazole (BTA) derivatives are not valid substrates because they form diazonium salt instead of diazo.[5] Thus, few examples have been reported using BTA derivatives to conduct triazole ring-opening chemistry. An alternative TA ring-opening approach is the radical reaction shown in Scheme 1B. Compared to the Dimroth rearrangement, an electron-withdrawing group is not required in this radical process, and both 2-triazolyl radical **A** and phenyl radical **B** are attractive intermediates with potentially interesting reactivity. However, due to the complex reaction nature (vide infra), there are very few studies reported regarding the radical reactivity moiety.[6] Herein, we report the first example of intermolecular azide radical addition to vinyltriazole and a sequential triazole ring-opening process. Imine nitrile and quinoxaline were prepared in good yields with excellent chemoselectivity, which further enriched the versatile reactivity of triazole in organic synthesis.

Scheme 1. Triazole Ring Opening Synthesis



During the last several years, our group has studied the coordination ability of TA toward transition metal cations.[7] To access different functional groups, we have developed new syntheses of various triazole derivatives.[8] One example was the vinyltriazole through gold-catalyzed TA addition to alkyne (Scheme 2).[9]

Our interest in developing a radical-promoted triazole ring opening was initiated from the "failed" vinyltriazole polymerization. As shown in Scheme 2, in our attempt to form triazole copolymer, no polymerization occurred under various radical conditions. Even "worse", polymerization of styrene was also shut down with the presence of only 5% vinyltriazole **1a**. This result suggested that vinyltriazole might quench radicals, likely through the formation of triazoyl radical **A′** (Scheme 2). Notably, although this new radical addition approach is attractive, the existence of multiple reaction paths is the main challenge and prevents the application of this strategy from any practical synthesis. To explore the reactivity of the triazoyl radical, we conducted reactions of **1** with various radical precursors using cerium ammonium nitrate as the oxidant. Interestingly, as shown

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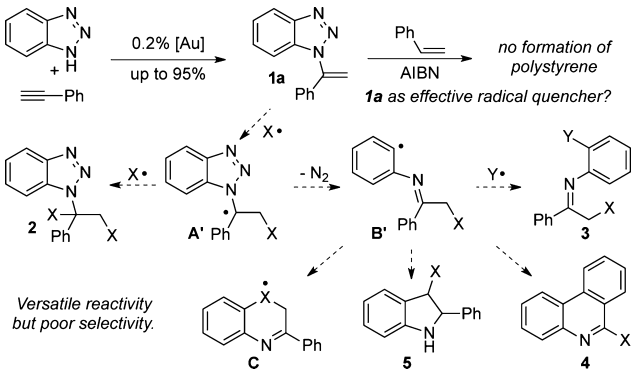
Scheme 2. Triazole Opening toward N-Heterocycle Synthesis



in Figure 1, these radical precursors ($NaSO_2CF_3$, $NaSO_2Tol$, NaSCN, NaBr, NaN_3, and $PhNHNH_2$) provided products **3a**–

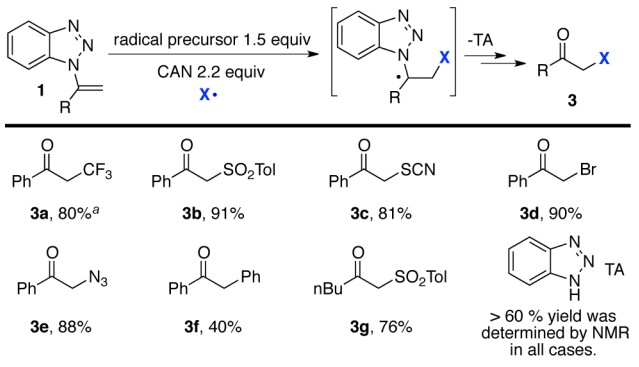
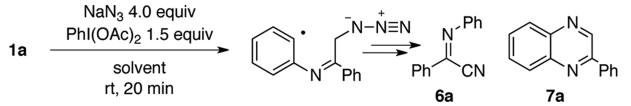


Figure 1. CAN-mediated radical addition to vinyltriazole. Standard conditions: **1** (0.2 mmol), CAN (0.44 mmol, and DMSO (4 mL) were mixed followed by the addition of radical precursor (0.3 mmol). Isolated yields. [a]NMR yield.

3f with good isolated yields. These results are exciting because they confirmed the feasibility of the proposed radical addition to vinyltriazole as a potential new reaction path under mild conditions. Some challenging substrates, such as the less reactive aliphatic vinyltriazole, could give the desired product **3g** in 76% yield, which greatly highlighted the advantage of this new approach.

The recovery of BTA in these reactions, however, confirmed that the radical-promoted triazole ring opening did not occur. It is possible that the radical intermediate **A′** was oxidized by CAN (to carbon cation) prior to TA ring opening. Thus, milder oxidants, such as hypervalent iodine compounds,[10] were used to react with **1**. Meanwhile, NaN_3 was selected because an azide radical can be formed easily in the presence of $PhI(OAc)_2$ and the newly formed organic azide can be an effective radical trap.[11]

As shown in Figure 2, nitrile[12] **6a** and quinoxaline **7a** were determined as the two major products. Notably, complete consumption of vinyltriazole was observed in all cases. Better yields were obtained with more polar dimethylsulfoxide (DMSO) as the solvent. It is possible that the solubility of NaN_3 accelerated the nitrile formation compared to the other reaction pathways. Finally, under diluted (0.033 M) conditions, product **6a** was isolated in 85% yield. This result was exciting as it gave the first example of radical addition for TA ring opening under mild conditions. Interestingly, under these reaction conditions, both quinoline **4** and indoline **5** were not observed.



conditions	conv	6a	7a	conditions	conv	6a	7a
DCM, 0.1 M	100%	25%	10%	DMSO, 0.1 M	100%	70%	<5%
DMF, 0.1 M	100%	55%	5%	DMSO, 0.033 M	100%	85%	<5%

Figure 2. Intermolecular radical addition for TA ring opening. Standard conditions: **1a** (0.2 mmol), $PhI(OAc)_2$ (0.3 mmol) and solvent were mixed followed by the addition of NaN_3 (0.8 mmol). NMR yields.

Screening of reaction scope is shown in Figure 3. This reaction worked well with α-aromatic-substituted vinyltriazole, including

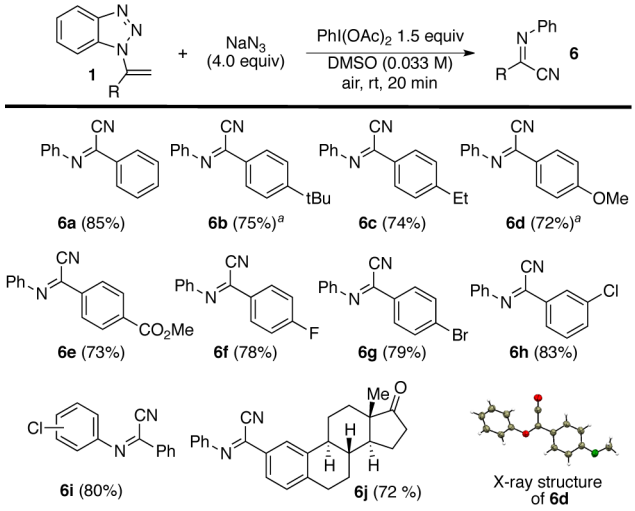


Figure 3. Substrate scope of nitrile **6**. Standard conditions: **1** (0.2 mmol), $PhI(OAc)_2$ (0.3 mmol) and DMSO (6 mL) were added, followed by NaN_3 (0.8 mmol). Isolated yields. **1i** was a mixture of 5-Cl and 6-Cl isomers. **6i** was same mixture of chloride isomers (1:1). Both isomers could not be isolated by column chromatography. [a]NaN_3 10.0 equiv was used.

tolerability of substituent groups with different electronic nature (**6a**–**6h**). The structure of **6d** was first confirmed by NMR and later unequivocally established by X-ray crystallography. When an electron-donating group was introduced (**6b** and **6d**), more NaN_3 was needed to improve the yield of nitrile formation. Aliphatic-substituted vinyltriazole gave complex reaction mixtures, likely caused by the electron-donating alkyne group and the potential elimination on the side chain. Finally, natural product derivative **6j** was obtained in 72% yield, which indicated a reasonable substrate scope, demonstrating the generality of this new reaction path. We then moved our attention to the formation of the metal-free denitrogenative transannulation product, quinoxaline **7**, which proceeded through an even more challenging azide radical cyclization path.

To better monitor the reaction by NMR, *para*-*t*-Bu-phenyl-substituted vinyltriazole **1b** and the easily handled $TMSN_3$ were used. To our surprise, metal-free denitrogenative transannulation product[13] quinoxaline **7b** was obtained as the major product (in $CDCl_3$) (nitrile **6b**, <5%), though with low yield (33%, Table 1, entry 2). Unfortunately, the addition of Brønsted acid (entry 3) or Lewis acid (entry 4) gave the proposed bis-azide **2b** as the major product.[14] Solvent screening confirmed DMSO as the optimal choice (entries 5–7). Finally, diluting the mixture to 0.01 M (suppressing undesired intermolecular pathways) gave

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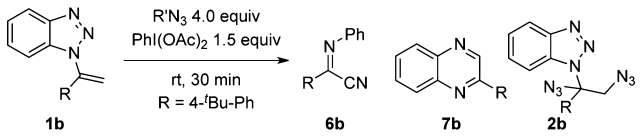
Table 1. Screening of Conditions[a]



entry	RN_3	solvent	addt.	concn (M)	conv (%)	yield (%)[b] 6b	7b	2b
1	NaN_3	DMSO	-	0.033	100	**75**	6	<5
2	$TMSN_3$	$CDCl_3$	-	0.1	100	<5	33	<5
3	$TMSN_3$	$CDCl_3$	TFA	0.1	100	<5	8	80
4	$TMSN_3$	$CDCl_3$	$Ga(OTf)_3$	0.1	100	<5	<5	90
5	$TMSN_3$	MeCN	-	0.1	100	<5	40	<5
6	$TMSN_3$	DMF	-	0.1	100	<5	30	<5
7	$TMSN_3$	DMSO	-	0.1	100	<5	55	<5
8	$TMSN_3$	DMSO	-	0.02	100	8	64	<5
9	$TMSN_3$	DMSO	-	0.01	100	8	**75**	<5
10	$TMSN_3$	DMSO	-	0.005	85	7	65	<5
11	$TMSN_3$	DMSO (60 °C)	-	0.005	50	7	45	<5
12	$TMSN_3$	DMSO	NaOAc (4.0 equiv)	0.01	100	58	16	<5
13	$TMSN_3$ (K_2CO_3 washed)	DMSO	-	0.01	100	12	72	<5

[a]Standard conditions: **1b** (0.2 mmol), $PhI(OAc)_2$ (0.3 mmol), and DMSO (20 mL) were mixed, then $TMSN_3$ (0.8 mmol) was added. [b]NMR yields.

the desired product **7b** with a 75% yield. Further dilution to 0.005 M resulted in lower conversion (85%) due to the slower reaction rate (relative to radical formation and quenching). Using a higher temperature (60 °C, entry 11) did not help the overall conversion due to the rapid radical quenching at elevated temperature. With the optimal conditions, the reaction scope was evaluated and summarized in Figure 4.

In general, good yields were observed, allowing this strategy to be a viable alternative synthesis for substituted quinoxaline under mild conditions. A wide scope of functional groups on both aromatic and aliphatic vinyltriazole was suitable for this reaction.

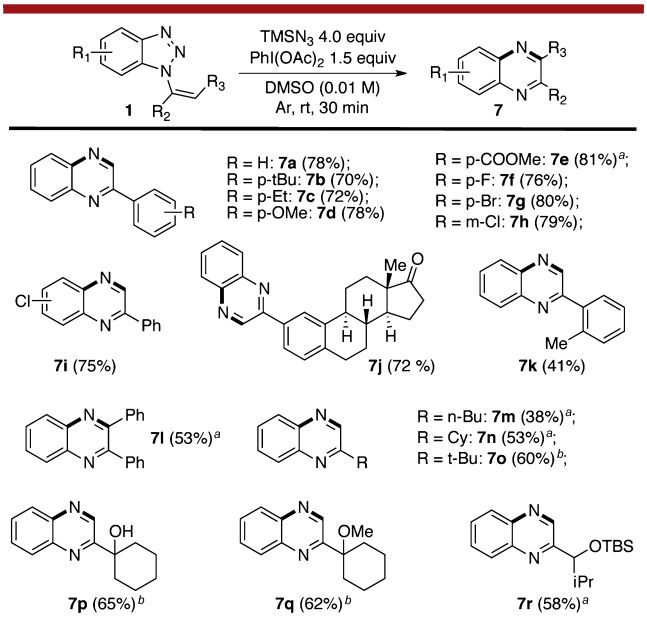
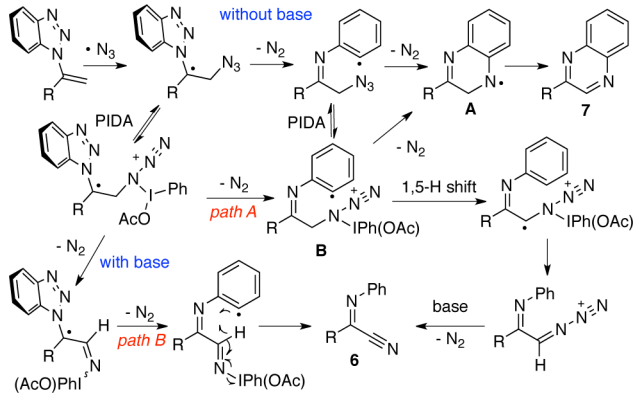


Figure 4. Substrate scope of quinoxaline **7**. Standard conditions same as Table 1. Isolated yields. **1i** was a mixture of 5-Cl and 6-Cl isomers. **7i** was same mixture of chloride isomers (1:1). Both isomers could not be isolated by column chromatography. [a]$PhI(OAc)_2$ (2.0 equiv) and $TMSN_3$ (4.0 equiv) were used. [b]Two milliliters of DMSO was used as solvent.

The α,β-disubstituted vinyltriazoles (synthesized from TA addition to an internal alkyne) could also proceed smoothly through this transformation (**7l**), though more azide was required due to the steric effect. The *n*-butyl-substituted vinyltriazole gave **7m** as the only isolatable product, though at low yield (38%), likely due to the rapid oligomerization side reactions. More bulky aliphatic-substituted vinyltriazoles gave significantly improved results (**7n**,**o**). Other functional groups, including hydroxyl, ether, and TMS, were all tolerated in this system (**7p**−**r**), highlighting the mild conditions of this transformation. Substrate with a substituent group on BTA, such as 5-chlorobenzotriazole, was still suitable and provided the corresponding product **7i** in 75% yield. Finally, natural product derivative **7j** was obtained in 72% yield.[15]

A plausible reaction mechanism is proposed in Scheme 3. The formation of quinoxaline **7** under neutral conditions was rather

Scheme 3. Proposed Mechanism: Chemoselective TA Opening



straightforward: radical addition to azide to form intermediate **A**. In contrast, the path to nitrile was less clear. First, the radical-promoted triazole ring opening followed by the 1,5-H shift of intermediate **B** (path A) looks very reasonable. However, from the experimental results, the basicity of NaN_3 is likely the determining factor for the nitrile formation.[16] Thus, path A is unlikely due to the lack of involvement of base in the rate-determining step. Moreover, bis-azide **2** was observed as the major byproduct, which suggested that the 2-triazolyl radical has reasonably good stability. Thus, base-mediated azide denitrogenation followed by radical-promoted triazole ring opening (path B) is more consistent with the experimental observation.

In summary, we report herein the first example of intermolecular radical addition to vinyltriazole as an alternative approach for triazole ring opening toward the synthesis of quinoxaline and imino nitrile. Without the triazole ring opening, a wide range of α-substituted ketones was obtained efficiently. The application of vinyltriazole as a radical trap provides a new approach to introduce the diversity of triazole activation under mild conditions. Applications of this radical-mediated triazole ring-opening strategy for other complex molecular syntheses are currently ongoing in our laboratory.

■ ASSOCIATED CONTENT

Supporting Information

Experimental details and NMR data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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