The Selectivity for Alkynyl- or Allenyl Imidamides and Imidates in Copper-Catalyzed Reactions of Terminal 1,3-Diynes and Azides

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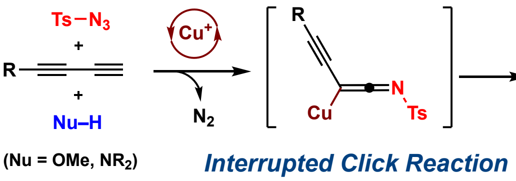
Supporting Information Placeholder



ABSTRACT: Copper-catalyzed reactions of terminal 1,3-diynes with electron-deficient azides to generate either 3-alkynyl or 2,3-dienyl imidamides and imidates are described. The selectivity depends on the diyne substituents and the nucleophile that reacts with the ketenimide intermediate generated from corresponding triazole precursor. Reactions of 1,3-diynes containing a propargylic acetate afford [3]cumulenyl imidamides while the reactions using methanol as trapping agent selectively generate 2,3-dienyl imidates. 5-membered heterocyles were obtained from 1,3-diynes containing a homopropargylic alcohol or amine substituent.

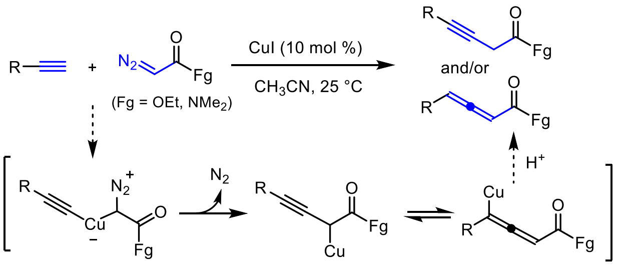
Allenes constitute a distinct class of organic compounds with two orthogonal π-bonds. There are numerous natural products and bioactive molecules that contain allene substructures.[1–3] It has been demonstrated that allene substituted bioactive compounds, like steroids,[4,5] prostaglandins,[6,7] carbacyclins,[7] nucleosides,[8] and unnatural amino acids[9] display higher potency, increased metabolic stability, and bioavailability. Because of the strained nature of the cumulene structure, allenes has been engaged in numerous synthetic transformations as a versatile building block to form a variety of carbo- and heterocyclic frameworks.[10–19] Axial-to-central chirality transfer is an efficient method to generate chiral compounds containing one or more stereogenic centers from chiral allenes.[19–22]

Due to the important utility of allenes, it is highly desirable to develop new synthetic methods to generate functionalized allenes from readily available starting materials.[23–28] One of the traditional approaches to synthesis of allenes involves 1,2-elimination of vinyl derivatives under strong basic or metal catalyzed conditions.[29] S_N2'-type reactions with propargylic alcohol derivatives (FG–CH_2–C≡C)[30–33] or isomerization of enyne moieties[34] also constitutes an efficient method to generate allenes. Transition metal-catalyzed coupling between terminal alkynes and carbonyl moieties in the presence of a secondary amine is also a well-established method[35] and a Cu(I)-catalyzed cross-coupling of terminal alkynes with diazo compounds is another efficient protocol to generate allenes.[36] Trisubstituted allenes can be accessed via metal catalysed cationic Heck coupling of alkynes with aryl halide/triflate.[37-39] Enones and ynones are also explored as a precursor of allenes.[40-41]

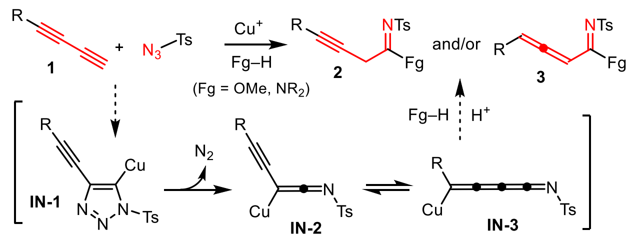
In 2004, Fu reported a Cu(I)-catalyzed coupling of alkynes and diazoacetate under mild conditions to generate 3-alkynyl carboxylate and only small amounts of the corresponding allenoates were observed (Scheme 1A).[42] On the other hand, Lee and others found that the alkynes containing a heteroatom substituent at the propargylic or homopropargylic carbon center preferentially generate the allenoate and especially in the presence of base such as triethyl amine, allenoate became the exclusive product.[43] Fox also reported a similar reaction that selectively generate allenoate as the product.[44] Although the exact mechanisms of these reactions are not well understood, on the basis of other related reactions, we propose a copper acetylide-mediated mechanism for the formation of the 3-alkynoate and allenoate. Relying on this copper acetylide-

Scheme 1. Two different approaches for the formation of closely related functional groups

A) Fu's Cu-catalyzed coupling of terminal alkyne and diazo compound



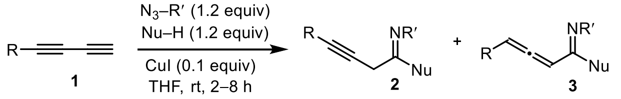
B) This work: Cu-catalyzed coupling of diyne and azide



mediated mechanism, we envision that the copper-catalyzed coupling of terminal 1,3-diyne **1** and azide would generate 3-alkynyl and allenyl imidamide/imidate **2**/**3** (Scheme 1B). We surmise that the terminal 1,3-diyne would form the corresponding copper acetylide, which will participate in a click reaction[45] with tosylazide to form triazole **IN-1**. Subsequent loss of molecular nitrogen will lead to two equilibrating organocopper aza-cummulenes **IN-2** and **IN-3**,[46] which then react with a nucleophile such as an amine or alcohol to generate imidamide[47] or imidate[48] containing either an alkyne (**2**) or an allene moiety (**3**). A unique feature of this transformation is that the selective transformation of the terminal alkyne moiety for the construction of imidamide and imidate functionality. Although starting from different set of starting materials, formation of closely related products from transformations in A and B is noteworthy. Herein describe our exploration of copper-catalyzed reactions of terminal 1,3-diyne **1** with tosylazide, which generated functionalized 1,3-di-substituted 2,3-dienyl imidamides and imidates **3** with good selectivity over the corresponding alkyne derivative **2**. Also, it was found that the type of nucleophiles, base additives, and the substituent patterns of the 1,3-diynes not only affect the ratio of **2** and **3** but also promote formation of alternative products such as [3]cumulenes and triple bond migrated products.

Our exploration commenced with assessment of the efficiency and selectivity for the formation 3-alkynyl and allenyl imidamide **2** and **3** (Table 1). Under the conditions employing copper catalyst (CuI, 10 mol%), azide (1.2 equiv), and amine (1.2 equiv), 1,3-diynes containing different substituent were examined. A hexyl-substituted terminal 1,3-diyne **1a** and TsN_3 provided a mixture of 3-alkynyl and allenyl imidamides **2aa** and **3aa** in 75% yield with a 2:1 ratio (entry 1). Reactions of **1a** with other azides such as diphenyl phosphoryl azide[49] and mesyl azide are also efficient affording 3-alkynyl imidamide **2ab** and **2ac** as the major product (entries 2 and 3). On the other hand, employing piperidine as a nucleophile under otherwise identical conditions, **1a** provided **2ad** exclusively (entry 4). 1,3-Diynes with a secondary (**1b**) or a tertiary alkyl group (**1c**) provided good yields of **2/3ba** and **2/3ca** but low selectivity with a slight preference for alkynyl product **2ba** and **2ca** (entries 5 and 6). 1-Cyclohexenyl substituted 1,3-diyne provided **2/3da** in 48% with a preference of compound **3da**. 1,3-Diyne **1e** containing a propargylic hydroxyl group afforded allene derivative **3ea** predominantly (entry 8), whereas 1,3-diyne **1f** containing a trimethylsilyl group provided alkyne derivative **2fa** selectively but in marginal yield (entry 9).

Table 1. Efficiency and product distribution with assorted nucleophiles, azides, and 1,3-diynes of different substituent



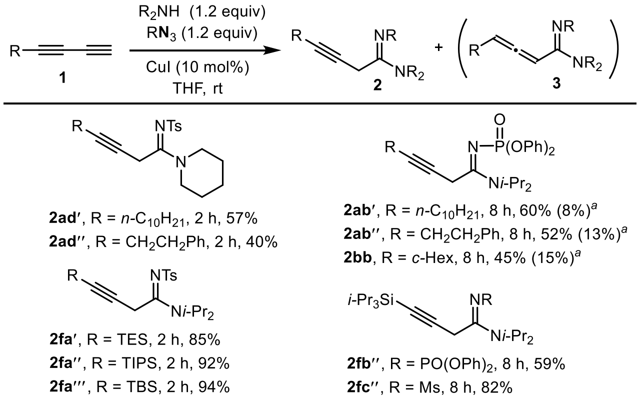
Entry	R	Nu–H	Azide	Yield % (alkyne:allene)[a]
1	**a**, *n*-Hex	*i*-Pr_2NH	TsN_3	**2/3aa**, 75% (2:1)
2	**a**, *n*-Hex	*i*-Pr_2NH	$(PhO)_2PON_3$	**2/3ab**, 66% (5:1)
3	**a**, *n*-Hex	*i*-Pr_2NH	MsN_3	**2/3ac**, 54% (2:1)
4	**a**, *n*-Hex	piperidine	TsN_3	**2ad**, 56% (1:0)[b]
5	**b**, *c*-Hex	*i*-Pr_2NH	TsN_3	**2/3ba**, 79% (2.3:1)
6	**c**, *t*-Bu	*i*-Pr_2NH	TsN_3	**2/3ca**, 71% (1.3:1)
7	**d**, 1-Cyclohex	*i*-Pr_2NH	TsN_3	**2/3da**, 48% (1:2.5)
8	**e**, CH_2OH	*i*-Pr_2NH	TsN_3	**2/3ea**, 73% (1:15)
9	**f**, $SiMe_3$	*i*-Pr_2NH	TsN_3	**2fa**, 45% (1:0)

[a] Isolated yield. [b] H_2O (1 equiv) and $NH_2OH\cdot HCl$ (1–2 mol%) were used as additives.

Once a general trend for the efficiency and selectivity between **2** and **3** has been revealed from the entries in Table 1, we next explored the selective formation of 3-alkynyl imidamide **2** (Scheme 2). As piperidine exclusively generated 3-alkynyl imidamide, reactions of *n*-decyl and homo-benzyl substituted 1,3-diynes with piperidine were performed, resulting corresponding 3-alkynyl imidamides **2ac′** and **2ac″** in 57% and 40% yield. Reaction with phosphoryl azide and alkyl substituted diynes predominantly generated 3-alkynyl imidamides (**2ab′**, **2ab″**, **2bb**) in moderate 45–60% yield. Electron-rich 1,3-diynes with silyl substituents selectively delivered 3-alkynyl imidamides. TES-, TIPS- and TBS-substituted 1,3-diynes provided the corresponding alkynyl derivatives **2fa′**–**2fa‴** in 85–94% yield. Reactions of TIPS-substituted 1,3-diyne with phosphoryl and mesyl azide also generated 3-alkynyl imides **2fb″** and **2fc″** exclusively in 59% and 82% yield. It is evident from Scheme 2 that reactions with cyclic amine, phosphoryl azide and electron-rich silyl-substituted 1,3-diynes tend to generate 3-alkynyl imidamide predominantly or exclusively.

Next, we examined reactions of different 1,3-diynes to selectively form 2,3-dienyl imidamide **3** (Scheme 3). Based on the initial observation with propargylic alcohol-containing diyne **1e** that selectively generated 2,3-dienyl imidamide, we further tested the reactivity of structurally diversified propargyl alcohols, (thio)ethers, amines, and amides. 1,3-Diynes containing secondary or tertiary alcohols afforded 2,3-dienyl imidamides (**3ga**, **3ga′**, **3ga″**, **3ga‴**, **3ja**, **3ja′**, **3ja″**, **3ka**) as a predominant or exclusive product in 65–76% yield. The selectivity between allenyl and alkynyl isomer depends on the substituent but no clear trend has been found. 1,3-Diynes with a tertiary alcohol and a cycloalkyl substituent delivered 2,3-dienyl imidamides (**3la**, **3la′**, **3la″**) in 70–80% yield with roughly a 10:1 selectivity. Carvone-containing 1,3-diyne afforded allene **3ma** (allene:alkyne = 7:1) in 69% yield with a

Scheme 2. Selective formation of 3-alkynyl imidamides with assorted nucleophiles, azides, and 1,3-diynes



2ad′, R = *n*-$C_{10}H_{21}$, 2 h, 57%
2ad″, R = CH_2CH_2Ph, 2 h, 40%

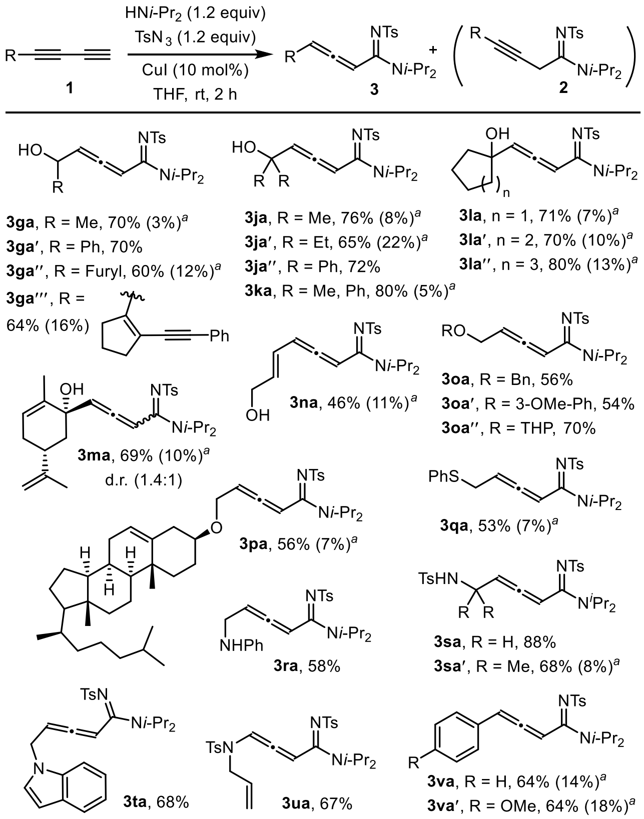
2ab′, R = *n*-$C_{10}H_{21}$, 8 h, 60% (8%)[a]
2ab″, R = CH_2CH_2Ph, 8 h, 52% (13%)[a]
2bb, R = *c*-Hex, 8 h, 45% (15%)[a]

2fa′, R = TES, 2 h, 85%
2fa″, R = TIPS, 2 h, 92%
2fa‴, R = TBS, 2 h, 94%

2fb″, R = $PO(OPh)_2$, 8 h, 59%
2fc″, R = Ms, 8 h, 82%

[a] Yields in the parenthesis represents the corresponding 2,3-dienyl isomer **3**.

Scheme 3. Formation of allenyl imidamides from diverse 1,3-terminal diynes



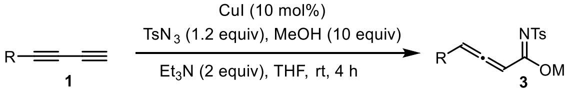
^{a} Yields in the parenthesis represents the corresponding 3-alkynyl compound **2**.

1.4:1 diastereomeric ratio. While a vinyl conjugated 1,3-diyne containing a free hydroxyl group provided allene **3na** in 46% yield with a low selectivity (4:1), 1,3-diynes with benzyl-, 3-MeO-Ph-, THP-protected primary alcohols exclusively generated allene derivative (**3oa**, **3oa′**, **3oa″**) in 54–70% yield. Similarly, a cholesteryl ether substituted 1,3-diyne generated allene **3pa** in 56% yield with a 8:1 ratio of allene:alkyne. On the other hand, the corresponding thioether afforded **3qa** contaminated with the alkyne isomer (allene:alkyne = 7.5:1). 1,3-Diynes containing an aniline and tosylamido substituent at the propargylic position selectively generated allenes **3ra** and **3sa** in 58% and 88% yield. A *gem*-dimethyl, however, lowered the yield and selectivity for **3sa′** (68%, 8:5:1). An indole substituted 1,3-diyne provided only allene **3ta** in 68% yield and *N*-allyl tosyl-substituted 1,3-diyne provided single isomer **3ua** in 67% yield. On the contrary, phenyl and 4-MeO-phenyl substituted 1,3-diynes provided moderate yield and selectivity providing allenes **3va** (64%, 4.6:1) and **3va′** (64%, 3.6:1).

Although the selectivity of forming allenyl imidamides is good, the formation of alkyne isomer could not be suppressed in many cases. At this juncture, we surmised that trapping the ketenimine intermediate with alcohols may have different product distribution.[50,51] Indeed, under identical conditions except for replacing i-Pr$_2$NH (1.2 equiv) with MeOH (10 equiv) and Et$_3$N (2 equiv), the reaction of 1,3-diynes selectively provided 2,3-dienyl imidates without a vestige of alkyne isomer (Table 2). Lower stoichiometry of methanol led to lower efficiency of the reaction. Alkyl and alkenyl diynes, which provided a mixture of allenyl and alkynyl imidamides previously, selectively generated allenyl imidates (**3ae**, **3ce**, **3de**) in moderate to good yield (entries 1–3). Even though 1,3-diyne **1g** containing free 2° alcohol led to decomposition (entry 4) the corresponding acyl-, benzyl-, and *tert*-butyldimethylsilyl-protected 1,3-diynes provided 2,3-dienyl imidates (**3he**, **3he′**,**3he″**) in good yield (entries 5–7). Similarly, 1,3-diyne with benzyl-protected 2° alcohol **1i** delivered 2,3-dienyl imidate **3ie** in 72% yield.

Subsequently, we observed that under standard conditions, 1,3-diynes **4** containing an acetoxy or benzoyloxy substituent at the propargylic position provided mono-, di-, and trisubstituted [3]cumulenes (Table 3).[52–56] For example, 1,3-diynes **4a**–**c** afforded trisubstituted cumulene **5a**–**5c** in 76–80% yield (entries 1–3). 1,3-Diynes substituted with a cycloalkyl moiety afforded the corresponding cumulenes **5d**–**5f** in good yield

Table 2. Synthesis of allenyl imidates by trapping with methanol



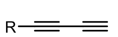
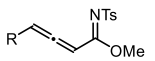
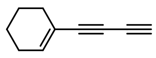
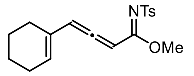
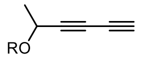
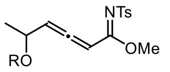
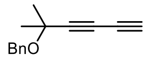
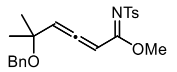
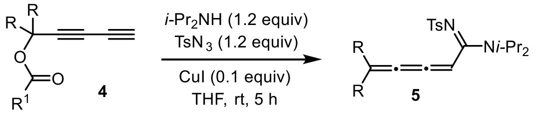
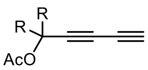
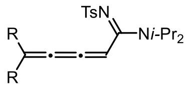
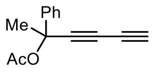
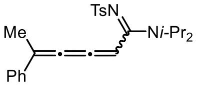
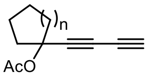
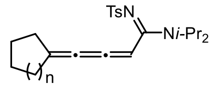
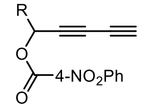
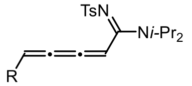
Entry	1,3-Diyne **1**		Allenyl imidate **3**		Yield (%)
1		**1a**, R = Hex		**3ae**	40
2		**1c**, R = *t*-Bu		**3ce**	52
3		**1d**		**3de**	64
4		**1g**, R = H		**3ge**	0
5		**1h**, R = Ac		**3he**	61
6		**1h′**, R = Bn		**3he′**	46
7		**1h″**, R = TBS		**3he″**	48
8		**1i**		**3ie**	72

Table 3. Synthesis of [3]cumulenyl imidamides via eliminating acetoxy or benzoyloxy group of putative allene intermediate



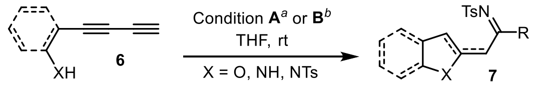
Entry	1,3-Diyne **4**		[3]Cumelene **5**		Yield (%)
1		**4a**, R = Me		**5a**	76
2		**4b**, R = Et		**5b**	79
3		**4c**		**5c**	80
4		**4d**, n = 1		**5d**	56
5		**4e**, n = 2		**5e**	82
6		**4f**, n = 3		**5f**	76
7		**4g**, R = H		**5g**	68
8		**4h**, R = Me		**5h**	74
9		**4i**, R = Ph		**5i**	77

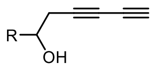
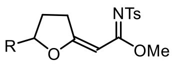
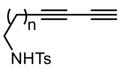
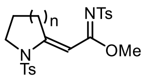
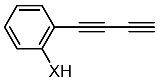
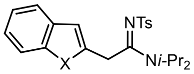
(entries 4–6). Unexpectedly, while the acetate derivative of tertiary alcohol afforded, the corresponding primary and secondary acetate provide a mixture of the expected [3]cumulenes and the corresponding acetoxy allene derivatives. However, upon replacing the acetate with *para*-nitrobenzoate (**4g**–**4i**), only cumulenes **5g**–**5i** were obtained (entries 7–9). We believe this is the consequence of a better leaving group capacity of a benzoate compared to an acetate. [3]Cumulene is a special class of polyene organic compounds whose synthetic utilities are little explored.[59-60] Thus, the current mild protocol to allow the preparation of [3]cumulenes containing various substituent patterns from readily available building blocks is of high synthetic utility.

We envision that with a suitably tethered nucleophile, the conversion of 1,3-diynes to the corresponding conjugated allenyl imidamide and imidates would promote an intramolecular Michael-type addition (Table 4).[61–65] Under standard conditions, homo-propargyl alcohol-containing 1,3-diynes **6a** and **6b** were smoothly converted to tetrahydrofuranylidene imidates **7a** and **7b** in 48% and 87% yield, respectively (entries 1 and 2). The corresponding homopropargyl sulfonamide **6c** led to 1-tosylpyrrolidinylidene imidamide **7c** in 72% yield (entry 3), however, forming 6-membered ring **7d** from **6d** failed (entry 4). 1,3-Diynes **6e** and **6f** substituted with a phenyl group containing an *ortho*-OH or NH_2 participated in the cascade reaction to generate benzofuranyl imidamide **7e** in 70% and indolyl imidamide **7f** in 64% yield, respectively (entries 5 and 6).

Although expected, migration of the triple bond from 3-alkynyl or 2,3-dienyl isomers to the corresponding 2-alkynyl isomer **8** was not observed under the conditions regardless of the reaction time. However, because of the thermodynamic preference for 2-alkynyl isomers, we surmised that the isomerization of **2** or **3** to **8** would happen if a stronger base than secondary amines is used (Scheme 4).[66] Indeed, treating a mixture of **2** and **3** with DBU (0.1 equiv) rapidly induced isomerization to provide 2-alkynyl imidamides **8a**–**8d**. On the other hand, phenyl- and silyl-substituted 3-alkynyl imidiamides **2** and **3** did not isomerize to the corresponding 2-alkynyl isomers **8e** and **8f**.

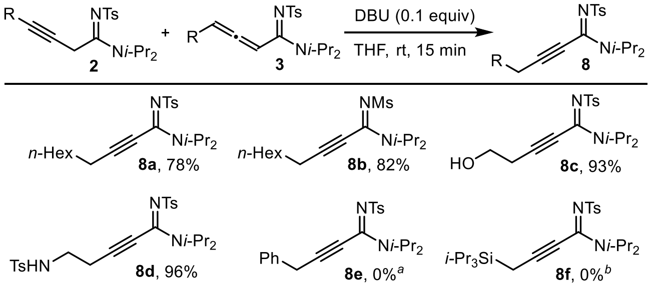
Table 4. Synthesis of heterocycles via intramolecular trapping of the putative allene intermediate



Entry	1,3-Diyne **6**		Conditions	Heterocycle **7**		Yield (%)
1		**6a**, R = H	A		**7a**	48
2		**6b**, R = Me	A		**7b**	87
3		**6c**, n = 1	A		**7c**	72
4		**6d**, n = 2	A		**7d**	0
5		**6e**, X = O	B		**7e**	70
6		**6f**, X = NH	B		**7f**	64

[a] Condition A: TsN_3 (1.2 equiv), Et_3N (2 equiv), MeOH (10 equiv), 12 h. [b] Condition B: TsN_3 (1.2 equiv), *i*-Pr_2NH (1.2 equiv), 4 h.

Scheme 4. Isomerization of 3-alkynyl and 2,3-dienyl imidamides to the corresponding 2-alkynyl isomers



[a] Decomposition of starting materials. [b] 3-Alkynyl imidamide **2** was recovered.

In conclusion, we have developed efficient protocols to generate discrete isomers of 2-alkynyl, 3-alkynyl, 2,3-dienyl, and 2,3,4-trienyl imidamides and imidates from copper-catalyzed reactions of 1,3-diynes and tosylazide. The selectivity between 3-alkynyl and 2,3-dienyl imidamides could be controlled by a heteroatom substituent at the propargylic position of the 1,3-diynes and employing different trapping reagent such as amines and alcohols. [3]Cumulene derivatives were also generated by employing 1,3-diynes that contain acetoxy or bezoyloxy substituent at the propargylic position. While trapping of the putative azacumulene intermediates with amines provided either 3-alkynyl or 2,3-dienyl imidamides depending on the structure of the trapping amines, trapping with methanol selectively generated 2,3-dienyl imidates. It was found that both 3-alkynyl and 2,3-dienyl imidamides could be isomerized to selectively generate the corresponding 2-alkynyl isomers under equilibrating conditions with stronger base such as DBU. Intramolecular trapping of the putative azacumulene intermediates provided 5-memebred heterocyclic products if 1,3-diyne substrates contain a homopropargylic hydroxyl or amino substituent. A unique feature of these unprecedented reactions is that under mild reaction conditions, terminal 1,3-diynes could be selectively converted to different unsaturated carboxylic acid derivatives with good selectivity.

ASSOCIATED CONTENT

Supporting Information

The Experimental procedures and spectroscopic data for all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org

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