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

Sourav Ghorai and Daesung Lee*

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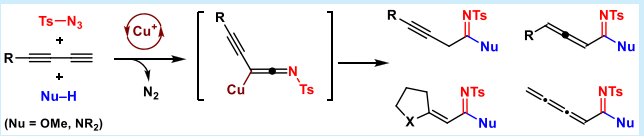
ABSTRACT: Copper-catalyzed reactions of terminal 1,3-diynes with electron-deficient azides to generate either 3-alkynyl or 2,3-dienyl imidamides and imidates are described. The selectivity depends on the diyne substituents and the nucleophile that reacts with the ketenimide intermediate generated from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

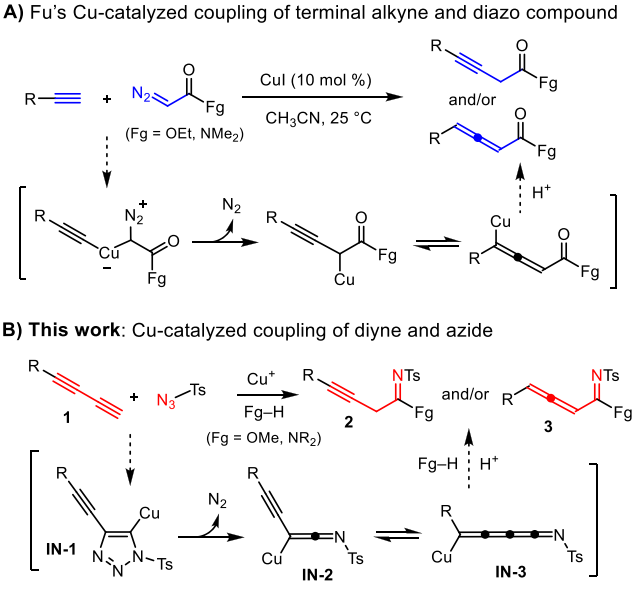


Allenes constitute a distinct class of organic compounds with two orthogonal π-bonds. There are numerous natural products and bioactive molecules that contain allene substructures.[1−3] It has been demonstrated that allene-substituted bioactive compounds, like steroids,[4,5] prostaglandins,[6,7] carbacyclins,[7] 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 have 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 for generating 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 the 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 ($FG-CH_2-C\equiv C$)[30−33] or isomerization of enyne moieties[34] also constitutes an efficient method for generating 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 for generating allenes.[36] Trisubstituted allenes can be accessed via metal-catalyzed 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 contrary, Lee and others found that the alkynes containing a heteroatom substituent at the propargylic or homopropargylic carbon center preferentially generate the allenoate, and in particular in

Scheme 1. Two Different Approaches to the Formation of Closely Related Functional Groups



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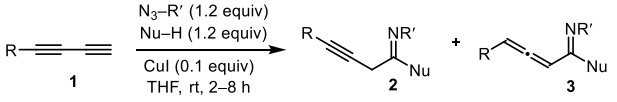
the presence of a base such as triethyl amine, allenoate became the exclusive product.[43] Fox also reported a similar reaction that selectively generated allenoate as the product.[44] Although the exact mechanisms of these reactions are not well understood, on the basis of other related reactions, we propose a copper acetylide-mediated mechanism for the formation of the 3-alkynoate and allenoate. Relying on this copper acetylide-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 [3+2] cycloaddition[45] with tosylazide to form triazole **IN-1**. The 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 the selective transformation of the terminal alkyne moiety for the construction of imidamide and imidate functionality. Although starting from a different set of starting materials, the formation of closely related products from transformations in A and B is noteworthy. Herein, we describe our exploration of copper-catalyzed reactions of terminal 1,3-diyne **1** with tosylazide, which generated functionalized 1,3-disubstituted 2,3-dienyl imidamides and imidates **3** with good selectivity over the corresponding alkyne derivative **2**. Also, it was found that the types of nucleophiles, the base additives, and the substituent patterns of the 1,3-diynes not only affect the ratio of **2** to **3** but also promote the formation of alternative products such as [3]cumulenes and triple-bond-migrated products.

Our exploration commenced with the assessment of the efficiency and selectivity for the formation of 3-alkynyl and allenyl imidamide **2** and **3** (Table 1). Under the conditions that include a copper catalyst (CuI, 10 mol %), an azide (1.2 equiv), and an amine (1.2 equiv), 1,3-diynes containing different substituents 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 products (entries 2 and 3, respectively). On the contrary, employing piperidine as a nucleophile under otherwise identical conditions, **1a** provided **2ad** exclusively (entry 4). 1,3-Diynes with a secondary (**1b**) or tertiary alkyl group (**1c**) provided good yields of **2**/**3ba** and **2**/**3ca** but low selectivity with a slight preference for alkynyl products **2ba** and **2ca** (entries 5 and 6, respectively). 1-Cyclohexenyl-substituted 1,3-diyne provided **2**/**3da** in 48% yield with a preference for 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).

Once a general trend for the efficiency and selectivity between **2** and **3** had 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 homobenzyl-substituted 1,3-diynes with piperidine were performed, resulting in the corresponding 3-alkynyl imidamides **2ac′** and **2ac″** in 57% and 40% yields, respectively. Reaction with phosphoryl azide and alkyl-substituted diynes predominantly generated 3-alkynyl imidamides (**2ab′**, **2ab″**, and **2bb**) in moderate 45−60% yields. 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% yields. 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% yields, respectively. 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). On the basis of 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

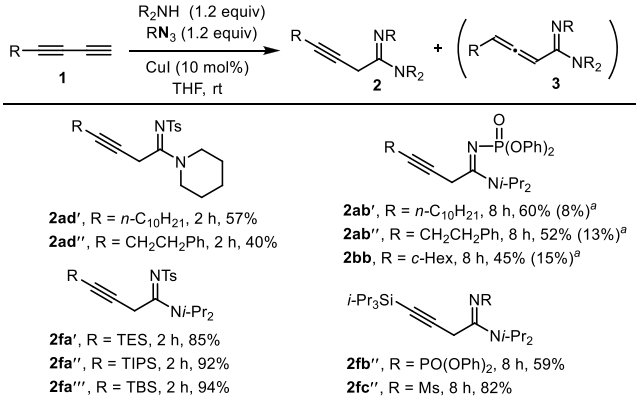
Table 1. Efficiencies and Product Distributions with Assorted Nucleophiles, Azides, and 1,3-Diynes of Different Substituents



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·HCl (1−2 mol %) were used as additives.

Scheme 2. Selective Formation of 3-Alkynyl Imidamides with Assorted Nucleophiles, Azides, and 1,3-Diynes



[a]Yields in parentheses represent those of the corresponding 2,3-dienyl isomer **3**.

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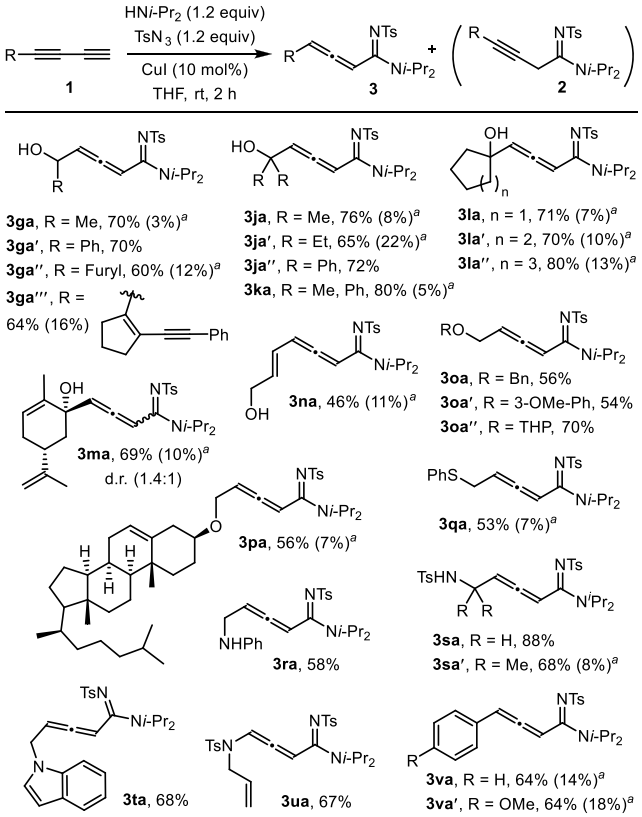
Scheme 3. Formation of Allenyl Imidamides from Diverse 1,3-Terminal Diynes

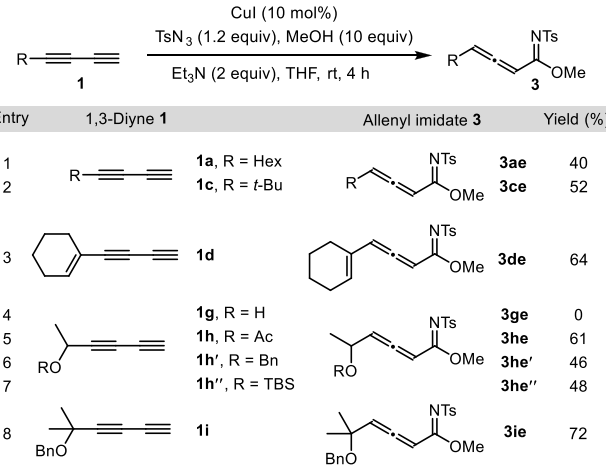


[a]Yields in parentheses represent those of the corresponding 3-alkynyl compound **2**.

amides. 1,3-Diynes containing secondary or tertiary alcohols afforded 2,3-dienyl imidamides (**3ga**, **3ga′**, **3ga″**, **3ga‴**, **3ja**, **3ja′**, **3ja″**, and **3ka**) as a predominant or exclusive product in 65−76% yields. The selectivity between the 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′**, and **3la″**) in 70−80% yields with a roughly 10:1 selectivity. Carvone-containing 1,3-diyne afforded allene **3ma** (7:1 allene:alkyne ratio) in 69% yield with a 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-, and THP-protected primary alcohols exclusively generated allene derivatives (**3oa**, **3oa′**, and **3oa″**, respectively) in 54−70% yields. Similarly, a cholesteryl ether-substituted 1,3-diyne generated allene **3pa** in 56% yield with an 8:1 allene:alkyne ratio. On the contrary, the corresponding thioether afforded **3qa** contaminated with the alkyne isomer (7.5:1 allene:alkyne). 1,3-Diynes containing aniline and tosylamido substituents at the propargylic position selectively generated allenes **3ra** and **3sa** in 58% and 88% yields, respectively. A *gem*-dimethyl, however, decreased 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 yields and selectivity provided 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 distributions.[50,51] Indeed, under identical conditions except for the replacement of *i*-Pr_2NH (1.2 equiv) with MeOH (10 equiv) and Et_3N (2 equiv), the reaction of 1,3-diynes selectively provided 2,3-dienyl imidates without a vestige of the alkyne isomer (Table 2). The lower stoichiometry of methanol

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

led to the 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**, and **3de**) in moderate to good yield (entries 1−3, respectively). Even though 1,3-diyne **1g** containing a free secondary alcohol led to decomposition (entry 4), the corresponding acyl-, benzyl-, and *tert*-butyldimethylsilyl-protected 1,3-diynes provided 2,3-dienyl imidates (**3he**, **3he′**, and **3he″**, respectively) in good yield (entries 5−7, respectively). Similarly, 1,3-diyne with benzyl-protected secondary alcohol **1i** delivered 2,3-dienyl imidate **3ie** in 72% yield.

Subsequently, we observed that under standard conditions, 1,3-diynes **4** containing an 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**−**4c** afforded trisubstituted cumulenes **5a**−**5c**, respectively, in 76−80% yields (entries 1−3, respectively). 1,3-Diynes substituted with a cycloalkyl moiety afforded the corresponding cumulenes **5d**−**5f** in good yields (entries 4−6, respectively). Unexpectedly, while the acetate derivative of tertiary alcohol was afforded, the corresponding primary and secondary acetates provide a mixture of the expected [3]cumulenes and the corresponding acetoxy allene derivatives. However, upon replacement of the acetate with *p*-nitrobenzoate (**4g**−**4i**), only cumulenes **5g**−**5i** were obtained (entries 7−9, respectively). We believe this is the consequence of the better leaving group capacity of a benzoate compared to that of an acetate. [3]Cumulenes make up a special class of polyene organic compounds whose synthetic utilities have been little explored.[57−60] Thus, the current mild protocol to allow the preparation of [3]cumulenes containing various

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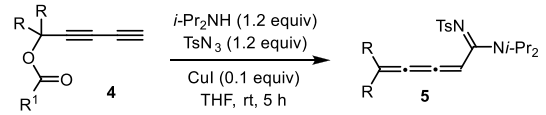
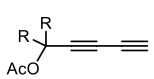
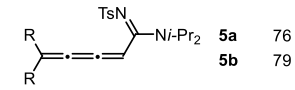
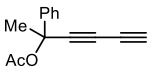
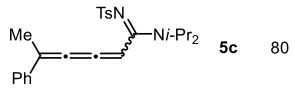
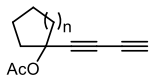
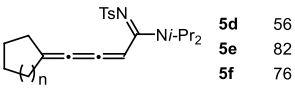
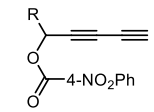
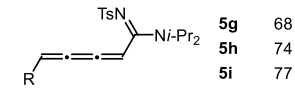
Table 3. Synthesis of [3]Cumulenyl Imidamides via Eliminating the Acetoxy or Benzoyloxy Group of a Putative Allene Intermediate

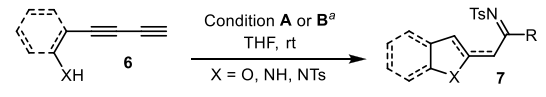


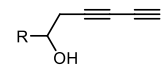
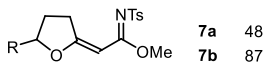
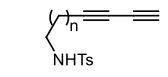
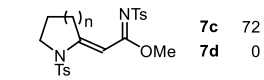
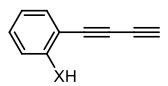
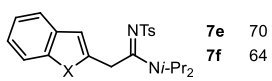
Entry	1,3-Diyne 4		[3]Cumulene 5		Yield (%)
1		4a, R = Me		5a	76
2		4b, R = Et		5b	79
3		4c		5c	80
4		4d, n = 1		5d	56
5		4e, n = 2		5e	82
6		4f, n = 3		5f	76
7		4g, R = H		5g	68
8		4h, R = Me		5h	74
9		4i, R = Ph		5i	77

substituent patterns from readily available building blocks is of highly synthetically useful.

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

Table 4. Synthesis of Heterocycles via Intramolecular Trapping of the Putative Allene Intermediate



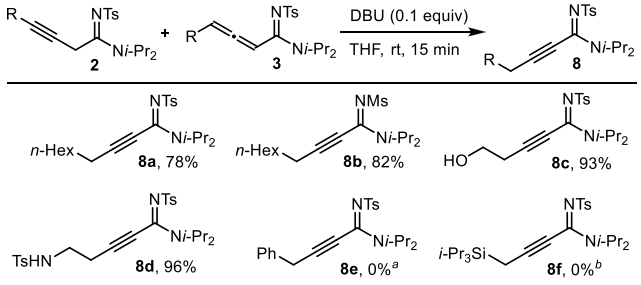
Entry	1,3-Diyne 6		Conditions	Heterocycle 7		Yield (%)
1		6a, R = H	A		7a	48
2		6b, R = Me	A		7b	87
3		6c, n = 1	A		7c	72
4		6d, n = 2	A		7d	0
5		6e, X = O	B		7e	70
6		6f, X = NH	B		7f	64

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

standard conditions, homopropargyl alcohol-containing 1,3-diynes **6a** and **6b** were smoothly converted to tetrahydrofuranylidene imidates **7a** and **7b** in 48% and 87% yields, respectively (entries 1 and 2, respectively). The corresponding homopropargyl sulfonamide **6c** led to 1-tosylpyrrolidinylidene imidamide **7c** in 72% yield (entry 3); however, the formation of a six-membered ring **7d** from **6d** failed (entry 4). 1,3-Diynes **6e** and **6f** substituted with a phenyl group containing an *o*-OH or NH_2 participated in the cascade reaction to generate benzofuranyl imidamide **7e** in 70% yield and indolyl imidamide **7f** in 64% yield (entries 5 and 6, respectively).

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 base stronger than secondary amines is used (Scheme 4).[66] Indeed, treating a

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.

mixture of **2** and **3** with DBU (0.1 equiv) rapidly induced isomerization to provide 2-alkynyl imidamides **8a**−**8d**. On the contrary, phenyl- and silyl-substituted 3-alkynyl imidiamides **2** and **3** did not isomerize to the corresponding 2-alkynyl isomers **8e** and **8f**, respectively.

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 reagents such as amines and alcohols. [3]Cumulene derivatives were also generated by employing 1,3-diynes that contain an 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 a stronger base such as DBU. Intramolecular trapping of the putative azacumulene intermediates provided five-membered heterocyclic products if the 1,3-diyne substrates contained 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 Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.orglett.0c03861.

Experimental procedures and spectroscopic data for all new compounds (PDF)

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AUTHOR INFORMATION

Corresponding Author

Daesung Lee − *Department of Chemistry, University of Illinois at Chicago, Chicago, Illinois 60607, United States;* orcid.org/0000-0003-3958-5475; Email: dsunglee@uic.edu

Author

Sourav Ghorai − *Department of Chemistry, University of Illinois at Chicago, Chicago, Illinois 60607, United States*

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.orglett.0c03861

Notes

The authors declare no competing financial interest.

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