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Letter

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

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depends on the divne substituents and the nucleophile that reacts with the ketenimide intermediate generated from the corresponding triazole precursor. Reactions of 1,3-diynes containing a

Nu-H (Nu = OMe, NR₂)

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.

llenes constitute a distinct class of organic compounds Π with two orthogonal π -bonds. There are numerous natural products and bioactive molecules that contain allene substructures.¹⁻³ It has been demonstrated that allenesubstituted 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-tocentral 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 metalcatalyzed conditions.²⁹ $S_N 2'$ -type reactions with propargylic alcohol derivatives $(FG-CH_2-C\equiv C)^{30-33}$ or isomerization of enyne moieties³⁴ 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 metalcatalyzed 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

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

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







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

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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 acetylidemediated mechanism, we envision that the copper-catalyzed coupling of terminal 1,3-diyne 1 and azide would generate 3alkynyl 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] cycloaddition⁴⁵ 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-3,⁴ which then react with a nucleophile such as an amine or alcohol to generate imidamide⁴⁷ or imidate⁴⁸ 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 1,3divne 1 with tosylazide, which generated functionalized 1,3disubstituted 2,3-dienvl 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 TsN₃ provided a mixture of 3-alkynyl and allenyl imidamides 2aa and 3aa in 75% yield with a

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

R—≡	= <u> </u>	N ₃ -R′ (1.2 equiv) Nu-H (1.2 equiv) Cul (0.1 equiv) THF, rt, 2-8 h	R NR' Nu 2	+ R NR'
entry	R	Nu-H	azide	yield (%) (alkyne:allene) ^a
1	a, <i>n</i> -Hex	<i>i</i> -Pr ₂ NH	TsN3	2/3aa, 75% (2:1)
2	a, <i>n</i> -Hex	<i>i</i> -Pr ₂ NH	$(PhO)_2PON_3$	2/3ab, 66% (5:1)
3	a, <i>n</i> -Hex	<i>i</i> -Pr ₂ NH	MsN ₃	2/3ac, 54% (2:1)
4	a, <i>n</i> -Hex	piperidine	TsN3	2ad , 56% (1:0) ^b
5	b, c-Hex	<i>i</i> -Pr ₂ NH	TsN3	2/3ba, 79% (2:3:1)
6	c, <i>t</i> -Bu	<i>i</i> -Pr ₂ NH	TsN3	2/3ca, 71% (1:3:1)
7	d, 1-cycloh	<i>i</i> -Pr ₂ NH ex	TsN3	2/3da, 48% (1:2:5)
8	e, CH ₂ OH	I <i>i</i> -Pr ₂ NH	TsN3	2/3ea , 73% (1:15)
9	f, SiMe ₃	<i>i</i> -Pr ₂ NH	TsN ₃	2fa, 45% (1:0)

 a Isolated yield. $^bH_2O~(1~equiv)$ and $NH_2OH\cdot HCl~(1-2~mol~\%)$ were used as additives.

2:1 ratio (entry 1). Reactions of 1a with other azides such as diphenyl phosphoryl azide⁴⁹ 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 1,3divne 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 vield (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

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**.

3-alkvnvl imidamide, reactions of *n*-decvl- and homobenzvlsubstituted 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 alcoholcontaining diyne **1e** that selectively generated 2,3-dienyl imidamide, we further tested the reactivity of structurally diversified propargyl alcohols, (thio)ethers, amines, and pubs.acs.org/OrgLett

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



^aYields 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-Divnes 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-divne 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-divnes with benzyl-, 3-MeO-Ph-, and THP-protected primary alcohols exclusively generated allene derivatives (30a, 30a', and 30a", 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*-Pr₂NH (1.2 equiv) with MeOH (10 equiv) and Et₃N (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





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-divnes 4 containing an an acetoxy or benzovloxy 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 pnitrobenzoate (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



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





standard conditions, homopropargyl alcohol-containing 1,3diynes **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 NH₂ 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 3alkynyl 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 coppercatalyzed 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-divnes 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

1 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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Notes

The authors declare no competing financial interest.

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