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Regioselective Rapid Synthesis of Fully Substituted 1,2,3-Triazoles Mediated by Propargyl Cations

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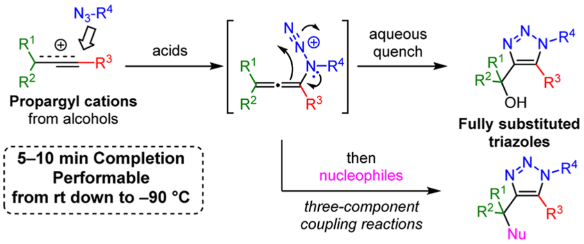
ABSTRACT



Regioselective rapid triazole syntheses at low temperature are described. Organic azides and propargyl cations generated by acids gave fully substituted 1*H*-1,2,3-triazoles. Most reactions could be performed in 5 min at not only rt but also −90 °C. Both terminal and internal alkynes were acceptable, and the sterically bulky substituents could afford the products smoothly. Various types of three-component coupling reactions were demonstrated, and the presence of allenylaminodiazonium intermediates was indicated.

Azide−Alkyne Cycloadditions (AAC) to produce 1,2,3-triazoles have been extensively developed since the copper-catalyzed conditions (CuAAC) were reported.[1] Due to their numerous applications especially in chemical biology,[2] ligand/material design,[3] and pharmaceuticals,[4] many groups have reported mild, rapid, and Cu-free triazolations (Scheme 1).[5] Recently, AAC using reactive strained alkynes have been well-utilized in chemical biology,[6] and C−C triple bond activations with carbonyls furnish [3 + 2] reactions under milder conditions compared to general alkynes.[7] However, CuAAC and metal-activated AAC are limited to mostly terminal alkynes, and most of the reported methods including classical Huisgen reactions require rt or higher with a long reaction time.[8,9] More recently, 1,2,3-triazoles have been focused on as synthetic precursors of functionalized compounds recently.[10,11] Therefore, novel methods of rapid

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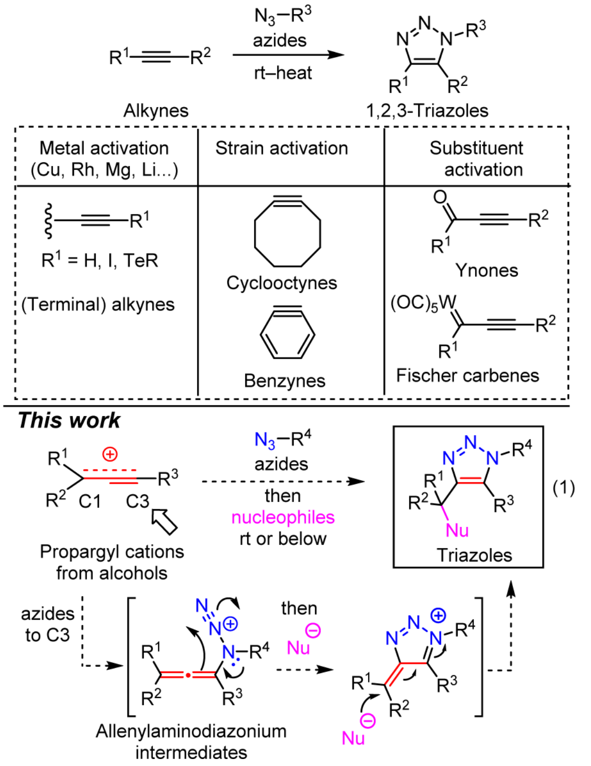
triazole synthesis should be studied, which allow use of internal and acyclic alkynes at rt or below.

We have recently developed a method for the synthesis of cyclic unsaturated imines by way of the reactions with allyl cations from allyl alcohols and organic azides.[12] Based on the conjugated carbocation chemistry, we herein report a rapid synthesis of highly substituted 1*H*-1,2,3-triazoles from propargyl cations and organic azides, which can accept both terminal and internal alkynes under low temperature and multicomponent coupling reactions.

Scheme 1. Strategies of Azide−Alkyne Cycloaddions and Our Approach



Our strategy for triazole synthesis is shown in eq 1. Using propargyl cations prepared from alcohols, reactions with azides at C3 could generate the allenylaminodiazonium intermediates powerful enough to form triazole rings immediately. Although it is known that allenyl azides gradually cyclize into triazoles at rt,[13] the chemistry of these diazonium compounds have been not reported to the best of our knowledge. However, we expected that these unstable species could achieve rapid transformations at ambient temperature. Due to the strong reactivities of both propargyl cations and diazonium intermediates, trisubstituted triazoles functionalized with additional nucleophiles could be obtained. Although concerted [3 + 2] reactions would deliver both 1*H*- and 3*H*-triazoles, deactivation of the C2 position by a delocalized carbocation can avoid this pathway and yield products selectively.

Our plan is challenging from the following viewpoints: (1) with azides, an sp^2 carbocation (C1) is more reactive than the desired sp carbocation (C3)[14a−c] to produce unsaturated imines by a Schmidt reaction[15] or propargyl azides;[13] (2) Meyer−Schuster rearrangement producing enones would be competitive;[14d] To avoid the reaction at C1 by steric and electronic influences,[16] we designed diphenyl propargyl

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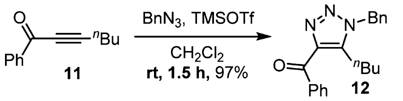
(9) Even in the presence of azides and acids, the [3 + 2] reaction of ynone **11** required a few hours at ambient temperature (eq 3).



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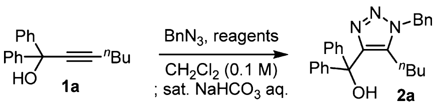
alcohol **1a** for the initial study of reaction conditions, and the reactions were quenched with a saturated sodium bicarbonate aqueous solution in order to produce triazolylalkanols, recently reported as new synthetic precursors (Table 1).[11]

Table 1. Optimization of Reaction Conditions

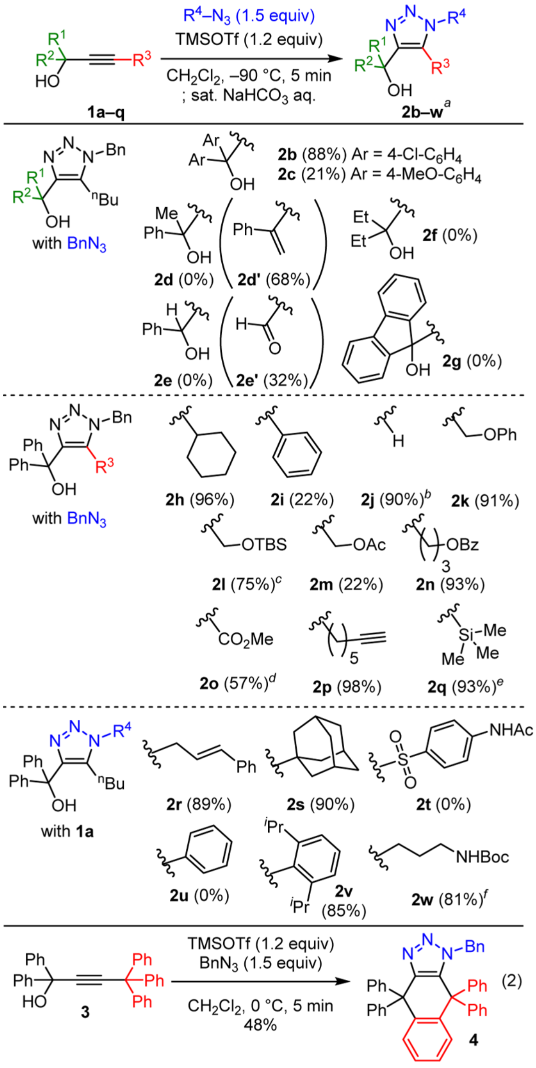


entry	BnN_3 (equiv)	reagent (equiv)	temp (°C)	*t* (min)	yield (%)[a]
1	2.5	$TsOH\cdot H_2O$ (1.2)	rt	20	11
2	1.5	MsOH (1.2)	rt	10	79
3	1.5	TMSCl (1.2)	rt	120	0
4	1.5	$FeCl_3$ (1.2)	rt	5	0
5	1.5	$Sc(OTf)_3$ (1.2)	rt	5	52
6	1.5	$Cu(OTf)_2$ (1.2)	rt	10	47
7	1.5	$BF_3\cdot OEt_2$ (1.2)	rt	1	90
8	1.5	$BF_3\cdot OEt_2$ (1.2)	−20	5	92
9	1.5	$BF_3\cdot OEt_2$ (1.2)	−60	5	80
10	1.5	TMSOTf (1.2)	−78	5	97
11	1.5	TMSOTf (1.2)	−90	5	99
12	1.2	TMSOTf (1.2)	−90	5	90
13	1.5	TMSOTf (1.05)	−90	5	94
14	1.5	TMSOTf (0.2)	−90	120	16
15	1.5	TBSOTf (1.2)	−90	5	60
16[b]	1.5	TMSOTf (1.2)	−90	5	88
17[c]	1.5	TMSOTf (1.2)	−90	5	97

[a] Isolation yield. [b] Performed in toluene. [c] High dilution conditions (0.005 M).

Tosylic acid gave a desired triazole **2a**, but the Meyer−Schuster rearrangement product was major probably due to its solubility and the presence of water of hydrates (entry 1).[12b,17,18] On the other hand, mesylic acid could produce **2a** in 10 min in good yield (entry 2). Although the conditions are effective at rt, further investigations on reagents were continued to improve the reaction speed and availability under low temperatures. Trimethylsilyl chloride (TMSCl) and ferric chloride only afforded a Meyer−Schuster rearrangement ketone (entries 3−4).[18] Scandium triflate and copper triflate worked to yield **2a** in moderate yield (entries 5−6), and a boron trifluoride ether complex worked well resulting in an excellent yield (entry 7). This reagent could complete the reaction in 1 min and was powerful enough to perform the reaction at −60 °C (entries 8−9). Further cooling conditions were achieved with TMSOTf, and the desired transformation was successfully demonstrated even at −90 °C, close to the melting point of the solvent (entries 10−11). It should be noted that these reaction conditions could afford **2a** in almost quantitative yield in only 5 min at −90 °C. Reducing the equivalence of benzyl azide and an acid reagent could also give similar results (entries 12−13). Unfortunately, catalytic conditions were ineffective probably due to the basicity of the resulting triazoles (entry 14). The use of TBSOTf also worked, but not as well as TMSOTf (entry 15). Instead of dichloromethane, toluene could work as an efficient solvent (entry 16). It is noteworthy that high dilution conditions did not reduce the efficiency of the reaction (entry 17). TfOH, $MgBr_2$, $Ti(O^iPr)_4$, $TiCl_4$, or $Yb(OTf)_3$ was not effective.

Scheme 2. Scope of Substituents on Alkynes and Azides[a]



[a] Isolation yield. [b] 2.1 equiv of TMSOTf was used. [c] Along with 7% of deTBS triazole. [d] Performed at −60 °C. [e] 10 min reaction. [f] 2.5 equiv of TMSOTf.

With optimal conditions determined, our focus was directed toward studying the substrates (Scheme 2), and the reaction temperature was set to −90 °C. From investigating the substituents on alcohols R^1 and R^2, electron-deficient aryl **2b** was found to be effective as a phenyl

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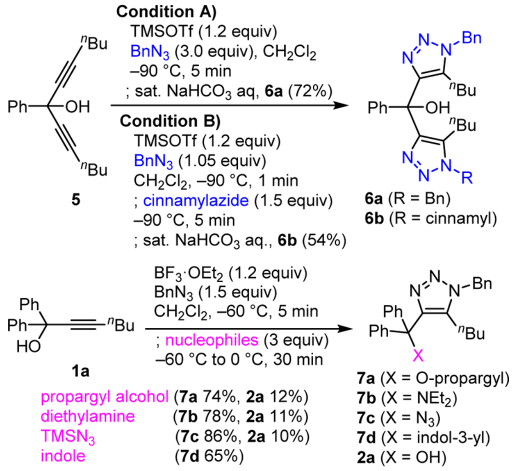
(17) $TsOH\cdot H_2O$ worked enough in the intramolecular reactions.

(18) Associated Meyer−Schuster reaction products were obtained as an inseparable mixture with unidentified byproducts. Thus, we did not isolate them to calculate yields.

Scheme 3. Three-Component Coupling Reactions

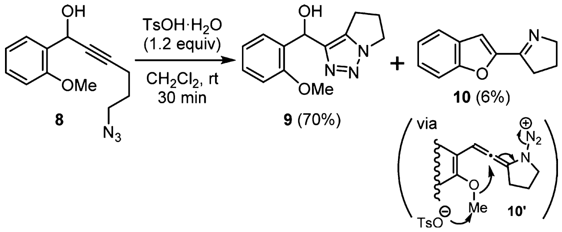


group, despite electron-donative aryl **2c** in low yield. Methylphenyl alcohol **1d** gave **2d′** in moderate yield as a dehydrated product. In the case of benzyl alcohol **1e**, aldehyde **2e′** was obtained probably through [3 + 2] followed by Schmidt reaction–hydrolysis.[14] Diethyl **1f** did not afford products **2f** in the intermolecular reactions, and fluorenyl alcohol **1g** was labile under acid conditions.

Upon further research of R^3, we found that despite conjugated alkyne **1i** and propargyl acetate **1m** resulted in fair yields, secondary alkyl **1h**, alkoxy methyl **1k–l**, and methoxycarbonyl **1n** afforded triazoles in good to excellent yields. Interestingly, terminal alkyne **1j** was also acceptable in giving disubstituted triazole **2j**, and the propargylic alkyne was selectively reacted in the case of **1p**.[19] Even sterically bulky compound **1q** could give [3 + 2] product **2q** immediately. In the case of trityl compound **3** (eq 2), triazolation followed by the Friedel–Crafts reaction occurred to give tricyclic product **4**.[20]

From screening R^4 in organic azides, it was revealed that although electrophilic azide and conjugated azide did not produce products, primary and tertiary azides afforded trisubstituted triazoles **2r–s**, and **2w**. In contrast to unreactive phenyl azide, sterically hindered 2,6-diisopropylphenylazide successfully gave desired **2v** due to the stronger nucleophilicity of its azide moiety than phenylazide as reported by Hosoya et al.[21] It should be noted that all triazoles were obtained as single isomers even in the case of ester **2o**.[22]

Scheme 4. Intramolecular Reaction



To develop the efficiency of our method, we conducted various types of three-component coupling reactions (Scheme 3). Double [3 + 2] reaction with dialkyne **5** furnished **6a** under condition A, and the reagent control (condition B) could also smoothly produce **6b**, a sequentially coupled product. Not only a hydroxy group but also other fuctional groups could be introduced by changing quenching methods. These were actually demonstrated to yield **7a–d** by the addition of trapping reagents.[23] The successive propargylation and azidation can also provide new junctures with other molecules through AAC reactions. With diethylamine and indole, a tertiary amine and quaternary carbon center was successfully constructed in one pot. Since the use of TMSOTf slightly increased the yield of **2a**, the resulting silanols or triflates would also be hydroxy group sources.

The presence of the envisaged allenylaminodiazonium intermediates was suggested by the intramolecular reaction in Scheme 4.[17] 2-Methoxyphenyl secondary alcohol **8** was transformed to bicyclic triazole **9** and benzofuranylpyrroline **10**. Since **10** was not obtained from **9**, **10** would be generated from **10′** through umpolung cyclization of an allenamine derivative[24] followed by demethylation of the oxonium ion.

In conclusion, we have developed regioselective rapid azide–alkyne cycloaddition to produce fully substituted 1*H*-1,2,3-triazoles. Use of propargyl cations derived from corresponding alcohols by acids or silylation reagents produced triazoles within 5–10 min through regioselective azidations. The cycloaddition reactions were performable not only at room temperature but also at −90 °C. Various types of three-component coupling reactions were demonstrated, and the presence of allenylaminodiazonium intermediates was indicated. Our method can provide an extension of the preparation of triazoles and their uses in synthetic organic chemistry.

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Supporting Information Available. Reaction procedures, preparations, and analytical data of all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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(20) (a) Although excess use of TMSOTf could afford **4** at −90 °C in 99% yield, the consumption of starting material was irreproducible. (b) Triazolylalkanol by [3 + 2] (no Friedel–Crafts reaction) was not observed.

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(22) The regiochemistry of the resulting triazoles were determined by NOEs and/or X-ray crystallographic analyses. CIF files of triazoles **2b**, **2h**, **2j**, **2q**, **2s**, **4**, and **7d** (CCDC 950501–950506 and 956342) are available free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

(23) Conversions of **2a** to **7a–d** were not observed under the same conditions.

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The authors declare no competing financial interest.