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COMMUNICATION

PIDA/TBAB-Promoted Oxidative Geminal Dibromofunctionalization of Alkynes: Direct Synthesis of Geminal Diazides

Sagar Arepally[a], Venkata Nagarjuna Babu[a], Ashok Polu[a] and Duddu S. Sharada[a]*

Abstract: PIDA/TBAB-promoted oxidative geminal diazidofunctionalization of alkynes has been described for the first time. The transformation demonstrates a mechanistically distinctive approach to access geminal diazides, in which TBAB plays a crucial role as brominating agent and in insitu generation of tetrabutylammonium azide. Further, we have demonstrated here the first cycloaminative strategy by tactically employing the two azides groups leading to quinoxalines and synthesis of bis-triazole derivatives via copper catalysis.

Introduction

Organic azides serve as highly privileged compounds due to its inherent reactivity and have found broad applications in biological,[1] pharmaceutical[2] and materials science fields[3] and are versatile precursors for the synthesis of N-containing heterocycles and functional group transformations.[4] For example, Huisgen "click" cycloadditions and Staudinger ligation reactions are routinely used in chemical biology.[5] Therefore, the development of practical and efficient approaches for the synthesis of functionalized organic azides is highly sought after. In this direction, readily available alkynes serve as potential building blocks for the preparation of organic azides.[6] Among which, difunctionalization of alkynes by simultaneous introduction of various functional groups across the triple bond has attracted great attention in recent years.[7] In particular, reductive azido-functionalization of alkynes is highly appealing owing to the importance of resulting products in chemical biology, drug discovery and various synthetic transformations.[8] However, most of the reports on direct one-step difunctionalization of the alkynes resulted in only olefins.[6] A general methodology is still lacking for the complete reductive azido-functionalization of triple bond of alkynes to provide functionalized alkanes. Pioneering work in this context, Yanada *et al*.[9] have reported the synthesis of diazidoketones (geminal diazides) by reaction of aryl alkyl alkynes, N-iodosuccinimide (NIS) and $TMSN_3$ (Scheme 1a). However, lack of wide substrate scope limits their application. Recently, Kirsch and co- workers realized for the synthesis of the geminal diazides *via* direct diazidation of 1, 3-dicarbonyls.[10] However, there have been limited number of methods known for the synthesis of geminal diazides.[11] Consequently, the development of efficient strategy for the installation of multiple azide functionalities into new molecules at one carbon is highly challenging.

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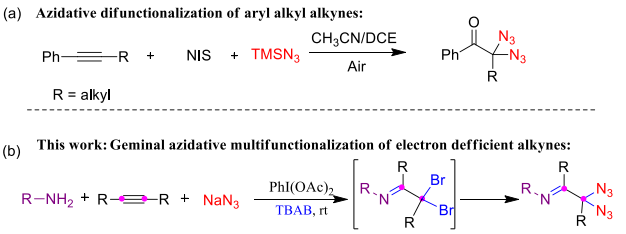
Moreover, constructing these molecules from ample starting materials is of great importance. Herein we disclose an unprecedented phenyliodine diacetate (PIDA)/tetrabutylammonium bromide (TBAB) promoted oxidative geminal dibromofunctionalization of alkynes with primary amines and sodium azide (Scheme 1b) through distinctive mechanism to access α,α-diazido β-iminoester derivatives. As far as we know, this method demonstrates the first example of PIDA/TBAB promoted diazidofunctionalization of electron deficient alkynes to access synthetically and biologically valuable geminal diazide substrates. Literature survey showed that the reactivities of geminal diazides have not been much established though only a few members of which have been known.[9,12] Apart from these reports, their utilization for heterocycles synthesis is not much explored.[13] In this context, we have also demonstrated the versatility of geminal diazides *via* a first cycloaminative approach towards quinoxalines and synthesis of bis-triazole derivatives under copper catalysis.

Recently, we have reported dehydrogenative N-atom installation into enamines promoted by organoiodine reagents leading to diverse heterocycles in a selective manner.[14] In these transformations, the intrinsic property of iodine (III) reagents enables to serve as an umpolung reagent or as an oxidant. During our investigations in previous nitrogen incorporation strategies, we have observed the interesting geminal diazide **3aa** formation in moderate yields (Table 1, entry 1) when tetrabutylammonium bromide (TBAB) was used. Encouraged by this result we focused on further investigations of geminal diazidative functionalization of alkynes. We reasoned that this selective chemical transformation in the presence of TBAB is due to the rapid geminal dibromination of enamine β $C(sp^2)$–H and subsequent replacement of bromides by the azide nucleophile (Scheme 3).



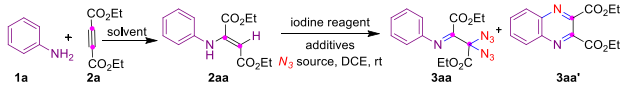
Scheme 1. Strategies for geminal diazido-functionalization of alkynes

Results and Discussion

Our studies begun to improve the yield of **3aa**. Initially, we examined the reaction with different equivalents of TBAB (Table 1 entries 2-5) in DCE as solvent, which indicates that TBAB is required in excess amount to furnish the product in good yield (entry 4). This supports our hypothesis of dibromination followed by formation of geminal diazides. To further check our assumption, we screened other tetrabutylammonium salts, which surprisingly did not furnish the desired geminal diazide product **3aa** (Table 1, entries 6-9),

instead we obtained the quinoxaline products via N-insertion. While other nucleophilic halogen sources like KI, NaCl and NH_4Cl also failed to afford **3aa** (Table S1, entries 1-3, see Supporting Information). From these experiments we can conclude that PIDA might be unable to oxidize the halide ions into halonium ions thus not affording the geminal dihalides and hence the desired geminal diazides. On the contrary, in the entries where we obtained quinoxalines along with geminal diazides (Table 1, entries 1-3), we did further investigations, wherein we subjected geminal diazides to optimized conditions which did not afford the quinoxalines. Thus ruling out the cycloaminative transformation of geminal diazides to quinoxalines (Scheme S1, eq7, see SI). Furthermore halonium sources such as NBS and NCS instead of TBAB also did not furnish the product **3aa** as we expected, however have afforded the N-insertion products **3aa'** (Table S1, entries 4 and 5, see SI).

Table 1. Optimization of the reaction conditions for the formation of α,α-diazido β-iminoester **3aa**[a]

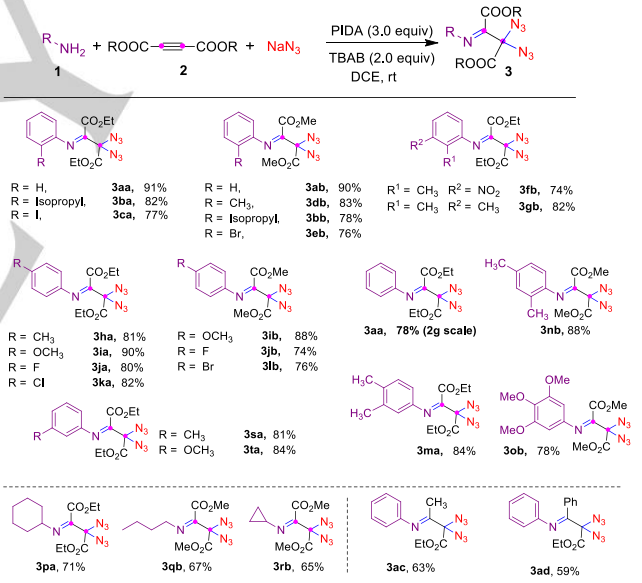


entry	iodine reagent (equiv)	[N_3] source (equiv)	additives (equiv)	yield (**3aa**%)[b]	yield (**3aa'**%)[b]
1	$PhI(OAc)_2$ (2.5)	NaN_3 (2.5)	TBAB (1.0)	55	15
2	$PhI(OAc)_2$ (2.5)	NaN_3 (2.5)	TBAB (0.5)	23	39
3	$PhI(OAc)_2$ (2.5)	NaN_3 (2.5)	TBAB (1.5)	61	12
4	$PhI(OAc)_2$ (2.5)	NaN3 (2.5)	TBAB (2.0)	74	-
5	$PhI(OAc)_2$ (2.5)	NaN3 (2.5)	TBAB (2.5)	75	-
6	$PhI(OAc)_2$ (2.5)	NaN3 (2.5)	TBAI (2.0)	-	65
7	$PhI(OAc)_2$ (2.5)	NaN_3 (2.5)	TBAF (2.0)	-	20
8	$PhI(OAc)_2$ (2.5)	NaN_3 (2.5)	TBACl (2.0)	-	43
9	$PhI(OAc)_2$ (2.5)	NaN_3 (2.5)	BTAC	-	62
10	-	NaN_3 (2.0)	TBAB (2.0)	-	-[c]
11	-	$TBAN_3$ (2.0)	-	39	-[d]
12	**$PhI(OAc)_2$ (3.0)**	**NaN_3 (4.0)**	**TBAB (2.0)**	**91**	-

[a]Reaction conditions: **1a** (1.0 equiv), **2a** (1.0 equiv), dry solvent (0.25 M), 25 °C, 14 h. [b]Isolated yields. [c]Hydroamination product isolated. [d]NBS (N-bromosuccinamide) (1.5 equiv) used as additive. TBACl = tetrabutylammonium chloride. BTAC = Benzyltriethylammonium chloride

In the absence of PIDA, the reaction did not proceed (Table 1, entry 10) indicating that PIDA's role as an oxidant for the azido-functionalization reaction. Although other combination[15] alternative to PIDA resulted in the **3aa**, the yield of the product was low (Table 1, entry 11). Lowering the amount of PIDA and sodium azide to 2.0 equiv decreased the yield to 65 % (Table S1, entry 6, see SI). Next, we have screened the reaction by increasing the equivalents of PIDA and NaN_3 (Table S1, entries 7-10, see SI). We are delighted to find geminal diazide **3aa** in 91% yield with 3.0 equiv of PIDA and 4.0 equiv of NaN_3 in DCE solvent (Table 1, entry 12). Among various iodine reagents examined, PIDA gave the product **3aa** in 91 % whereas other oxidants failed to give the desired product (Table S2, see SI). The use of other N_3-sources such as $TMSN_3$ and 1-azido-1,2-benziodoxol-3-(1H)-one IBA-N_3, and other combinations[15] in the absence of PIDA were not successful (Table S1, entries 11-15, see SI)). The solvent evaluation studies showed that DCE is the most suitable solvent (Table S3, entry 2, see SI). After optimization of the reaction conditions, we next examined the geminal diazidation reaction of amines **1** with different electron deficient alkynes **2** (Table 2). Different alkynes (**2a**, **2b**, **2c** and **2d**) were tolerated and gave the corresponding products (**3aa**-**3rb**, **3ac** and **3ad**) in good to excellent yields. Next, we turned our attention to test the broad range of aromatic amines **1**. Aromatic amines **1** containing electron-neutral and electron-rich functional groups have well reacted to afford the corresponding α,α-diazido β-iminoester derivatives (**3aa**, **3ba**, **3AB**, **3db**, **3bb**, **3gb**, **3ha**, **3ia**, **3ib**, **3ma** and **3nb**) in excellent yields. Electron-deficient halogen-substituted aryl amines worked well, provided the corresponding products (**3ca**, **3eb**, **3ja**, **3ka**, **3jb** and **3lb**) in very good yields. Slightly lower yields were observed for electron-withdrawing nitro- substituted aryl amine, which is due to less formation of enamine or hydroamination product (**3fb**). We sought to further explore this geminal diazidation reaction, to our delight, aliphatic amines were found to be compatible for hydroamination-diazide transfer reaction sequence (**3pa**, **3qb** and **3rb**). Furthermore, we explored the scope with those enamines which are not possible to generate insitu under mild conditions, which afforded the respective geminal diazide products in moderate yields (**3ac** and **3ad**). To validate the efficiency of this protocol, we carried out the gram-scale synthesis under optimized reaction conditions resulting in **3aa** in 78% yield.

Table 2. Substrate scope of amines and alkynes[a,b]

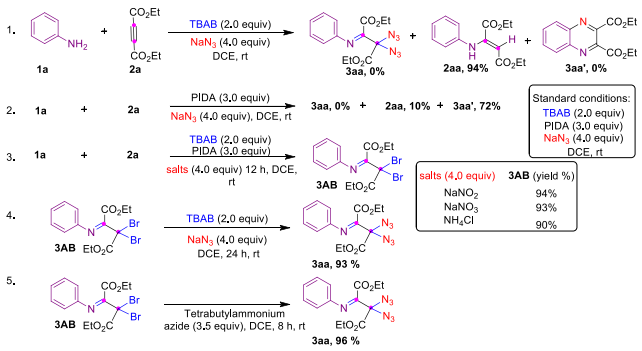


[a]Reactions were performed using **1a** (1.0 equiv), **2a** (1.0 equiv), PIDA (3.0 equiv), NaN_3 (4.0 equiv), TBAB (2.0 equiv) and dry DCE (0.25 M) at 25 °C for 8 to 14 h. [b]Yields after silica column chromatography.

Having demonstrated the scope of the protocol, a series of experiments were carried out to investigate this interesting reaction mechanism. The reaction has failed to furnish the desired product **3aa** in the absence of either PIDA or TBAB (Scheme 2, eq1 and 2), suggesting both PIDA and TBAB are crucial for this transformation. To investigate the possible radical pathway, we performed the reaction with 2,2,6,6-tetramethyl-1 piperidinyloxy (TEMPO) and 4-OH-TEMPO as radical inhibitors, which resulted in complex mixture with decreased yields of product **3aa** (21% and 25%) and enamine **2aa** (18% and 15%) (SchemeS1, eq1 and 2, see SI). However, the results are not conclusive as there is no complete inhibition of the

product **3aa** formation and the presence of unreacted enamine **2aa**. To further evaluate the radical pathway, we performed a radical clock experiment under standard conditions, which gave only the geminal diazide product **3rb**, and no other ring-opened coupling products were observed (eq3, see SI). These experiments suggested that reaction might proceed through the ionic mechanism.

Scheme 2. Control experiments



Accordingly, we assumed that bromide ion can be converted into bromonium ion by oxidant PIDA, which in turn undergoes electrophilic addition to enamine C(sp^2)–H resulting in the key intermediate **3AB**. To verify this possibility, we presumed to use other non-nucleophile sources such as $NaNO_2$ and $NaNO_3$ instead of NaN_3 to isolate intermediate **3AB**. Consequently, we obtained geminal dibromide **3AB** (Scheme 2, eq3). Then we next performed the reaction of geminal dibromide **3AB** with NaN_3, which failed to provide desired product **3aa** (eq4, see SI). To assess the role of PIDA and TBAB, we carried out few control experiments with geminal dibromide **3AB** (eq5, see SI). Among these experiments, only the reaction of **3AB** with NaN_3 and TBAB gave the geminal diazide **3aa** in 93% yield (Scheme 2, eq4). Furthermore, we performed the reaction of geminal dibromide **3AB** with tetrabutylammonium azide, which also resulted in geminal diazide **3aa** (Scheme 2, eq5). We have also performed the reaction under standard conditions with geminal dibromide **3AB**, which resulted only the geminal diazide **3aa** in 91% yield (eq6, see SI). These experiments and NMR experiments[16] suggested that TBAB is not only the brominating reagent but it also plays a key role in the nucleophilic replacement.

On the basis of above experimental results, and literature studies,[17] we proposed the plausible mechanism as shown in scheme 3. An oxidation of bromide ion by $PhI(OAc)_2$ in the presence of NaN_3 would provide the bromonium ion which undergoes a direct electrophilic addition to β-C(sp^2)-H of hydroamination product **I** to generate reactive intermediate **3AB**. The intermediate **3AB** would undergo nucleophilic replacement by basic N_3 anion from insitu generated tetrabutylammonium azide to afford the product **3aa**.

After successfully synthesis of geminal diazides, we have determined the thermal stabilities of few of selected compounds **3aa**, **3db**, **3ja**, **3ka** and **3ta** from DSC experiments in the regard of safety concerns when handling these diazides (TableS4, see SI).[10b,18] Accordingly, we have demonstrated their synthetic utility. Delightfully, we report herein a cycloaminative strategy in which the two-azide groups have been employed wherein one azide group serves as N-source by the formation of nitrene while another azide group is sacrificed for the aromatization resulting in quinoxaline derivatives **4a-4f** in good yields (Table 3). Geminal diazides with the unsymmetrically substituted aryl ring (**3sa**) furnished the mixture of isolable regioisomers (**4f and 4f'**). Further, the gram scale synthesis of quinoxalines also demonstrates the scalability and general applicability of this method.

Scheme 3. Plausible Mechanism

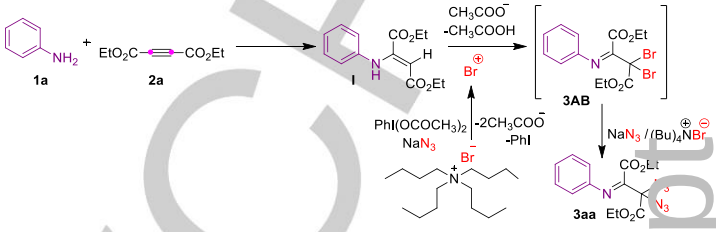
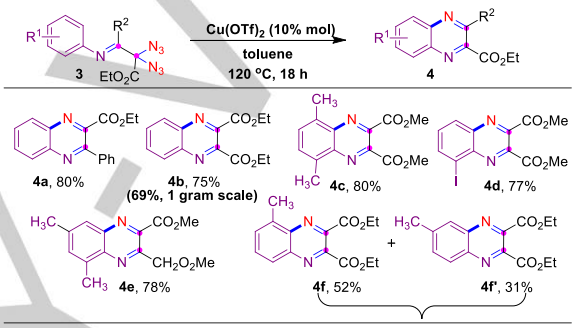


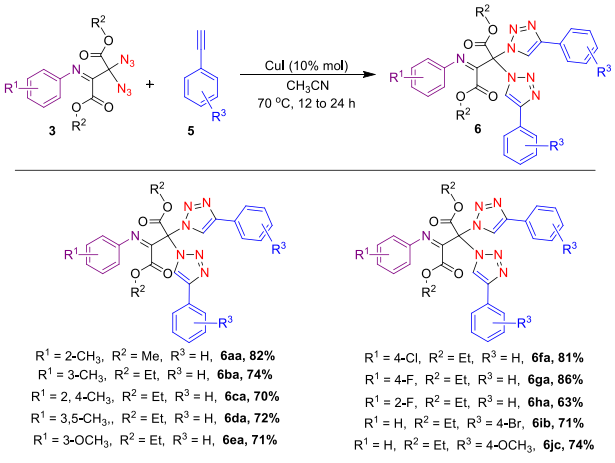
Table 3. Synthesis of quinoxaline compounds[a, b]



[a]Reactions were performed using **3** (1.0 mmol), $Cu(OTf)_2$ (10 mol%) and dry toluene at 120 °C for 18 h. [b]Isolated yields after silica column chromatography.

Furthermore, we have also presented the copper catalyzed azide-alkyne cycloaddition (click reaction) owing to the wide applications in material and surface sciences.[19] In this strategy, two azide groups of geminal diazides (**3a** to **3j**) reacted with terminal alkynes (**5a** to **5c**) to afford bis-triazole derivatives with very good (Table 4, **6aa** to **6jc**).

Table 4. Synthesis of bis-triazole compounds[a, b]



R^1 = 2-CH_3, R^2 = Me, R^3 = H, **6aa, 82%**
R^1 = 3-CH_3, R^2 = Et, R^3 = H, **6ba, 74%**
R^1 = 2, 4-CH_3, R^2 = Et, R^3 = H, **6ca, 70%**
R^1 = 3,5-CH_3,, R^2 = Et, R^3 = H, **6da, 72%**
R^1 = 3-OCH_3, R^2 = Et, R^3 = H, **6ea, 71%**

R^1 = 4-Cl, R^2 = Et, R^3 = H, **6fa, 81%**
R^1 = 4-F, R^2 = Et, R^3 = H, **6ga, 86%**
R^1 = 2-F, R^2 = Et, R^3 = H, **6ha, 63%**
R^1 = H, R^2 = Et, R^3 = 4-Br, **6ib, 71%**
R^1 = H, R^2 = Et, R^3 = 4-OCH_3, **6jc, 74%**

[a]Reactions were performed using **3** (1.0 mmol), **5** (2.5 mmol) and CuI (10 mol%) in CH_3CN at 70 °C for 12-24 h. [b]Isolated yields after silica column chromatography.

Conclusions

In conclusion, the first example of PIDA/TBAB-promoted geminal diazido-functionalization of alkynes under mild reaction conditions to access valuable α,α -diazide β-iminoester derivatives is disclosed here. The transformation features two azides and one amine groups transfer across the triple bond of alkyne to install two C-N bonds on each carbon in one reaction. This method demonstrates a mechanistically distinctive approach to complete reductive functionalization of alkynes by the addition of two different nucleophiles. Further, we explored the utility of synthesized geminal diazides in copper-catalyzed cycloamination for the synthesis of quinoxalines and bis-triazole derivatives. Further studies of geminal diazides are currently under way in our laboratory.

Experimental Section

Amine 1 (1 mmol) was taken in a dried 10 mL round bottom flask, and alkyne 2 (1 mmol) was added slowly in DCE (0.5 mL) solvent, and the reaction mixture was stirred (if required) at room temperature for 10 min to 3 h. After the formation of hydroamination product (confirmed by TLC); solvent DCE (0.25 M, based on hypervalent iodine), tertrabutylammonium bromide (TBAB) (2 mmol) and NaN_3 (4 mmol) were added, followed by addition of phenyliodo(III)diacetate (PIDA) (3 mmol) in portion wise for 30 min. The progress of the reaction was monitored by TLC till the reaction is completed (4-14 h). The reaction mixture was quenched by addition of saturated solution of $NaHCO_3$ and extracted with ethyl acetate, dried over $MgSO_4$, and concentrated in vacuo. The residue was purified through a silica gel column using petroleum ether/ethyl acetate (9.8:0.2) as eluent. All the compounds 3aa to 3ta were confirmed by FTIR, ^{1}H NMR, ^{13}C NMR and HR-MS spectral analyses.

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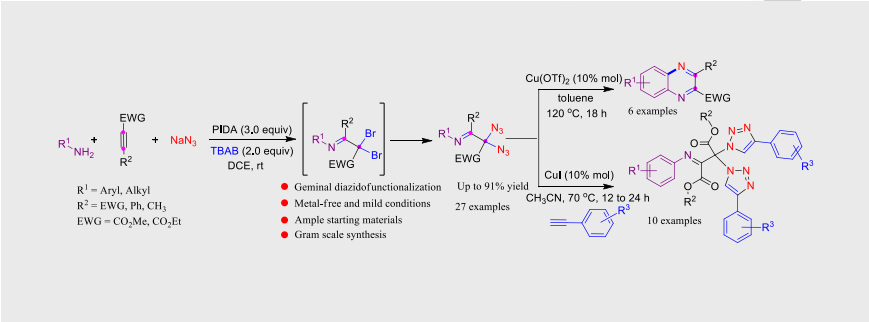

Organic Azides

Sagar Arepally, Venkata Nagarjuna Babu, Ashok Polu and Duddu S. Sharada

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PIDA/TBAB-Promoted oxidative Geminal Dibromofunctionalization of Alkynes: Direct Synthesis of Geminal Diazides

PIDA/TBAB-promoted oxidative geminal dibromination-diazidation sequence provides straightforward access to geminal diazides. In this transformation, TBAB plays a crucial role as brominating agent and in insitu generation of tetrabutylammonium azide. Further, we have presented the synthetic utility of geminal diazides by the synthesizing quinoxalines and bis-triazoles *via* copper catalysis.