Highly Selective Syn Addition of 1,3-Diones to Internal Ynamides Catalyzed by Zinc Iodide

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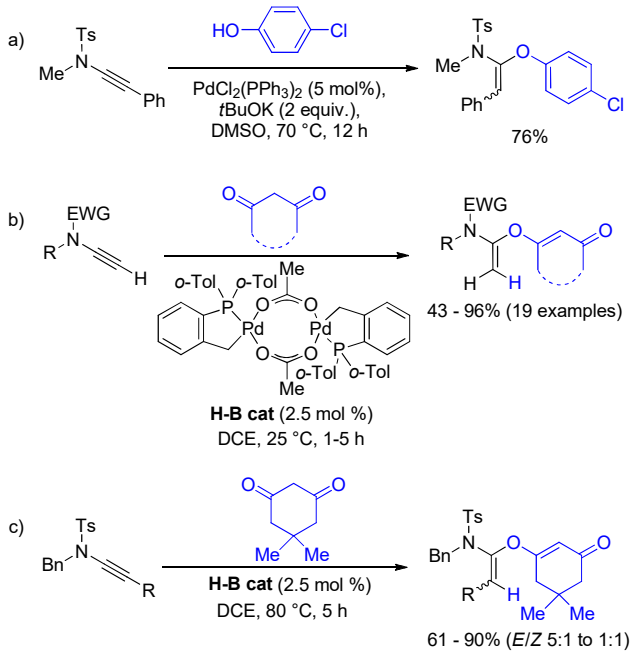
Dedication ((optional))

Abstract: Having previously established that 1,3-diones could be used as nucleophiles to perform additions to ynamides, highly selective hydroalkoxylation of internal ynamides is now described herein. Several catalytic systems were compared to carry out this transformation including transition metal-based catalysts or Lewis acids. ZnI_2 was found to be both very active and highly selective giving only *E* adducts through a *syn* addition. Scope and limits investigation showed that this catalyst was compatible with various functional groups. In addition to 17 examples of ynamide hydroalkoxylation, one example of ynamide hydroarylation is reported.

Introduction

Among the myriad of reactions using ynamides as substrate,[1] those consisting of the heteronucleophile introduction to the ynamide α-carbon are particularly interesting from a synthetic point of view. Thus, according to the nature of the nucleophile, as well as the pending functional groups of the ynamides, various structurally different products can be formed. With oxygen nucleophiles, various reactions can be performed[2-4] such as the hydration of ynamide that can be achieved under acid conditions to straightforwardly give rise to functionalized amides.[5] Skrydstrup even reported a gold-catalyzed hydration of dimerized ynamides leading to the formation of 2,5-diamidofurans.[6] Subsequently to Lam's report on palladium-catalyzed hydroacyloxylation of ynamide,[7] it was demonstrated that the addition of carboxylic acids could be performed without catalyst.[5b,8]

In comparison to the previously cited reactions, the hydroalkoxylation of ynamides has been less studied whereas it represents a straightforward access to unprecedented alkoxy-substituted enamide patterns. Unfortunately with simple alcohols, such as benzyl alcohol, hydroalkoxylation was unsuccessful.[9,10] Hsung disclosed that with allylic[11] and propargylic alcohols[12] the hydroalkoxylation was possible using a substoichiomietric amount of *p*-nitrobenzenesulfonic acid under thermal activation. However, since [3,3]-sigmatropic rearrangements took place, only the corresponding amides were isolated.[13] Very recently, Swamy reported a single example of hydroxyalkylation of an ynamide with phenol using a palladium-based catalyst and a base upon thermal activation.[14] Unfortunately, the stereochemistry of the carbon-carbon double bond was not clearly discussed (Scheme 1.a). During the course of our research directed toward the use of ynamides in [2+1] cycloadditions,[15] we discovered that Herrmann-Beller catalyst (**H-B cat**) was able to promote the hydroalkoxylation of ynamides with 1,3-diones.[16] Although good yields were obtained with terminal ynamides (Scheme 1.b), the resulting products were easily hydrolysable under acid conditions. With internal ynamides, alkoxy-substituted enamide adducts were significantly more stable to acid conditions but their preparation led to mixtures of *E*- and *Z*-isomers in low to moderate ratios (Scheme 1.c).



Scheme 1. Hydroalkoxylation reactions of ynamides affording alkoxy-substituted enamides.

To investigate the synthetic potential of alkoxy-substituted enamides,[8b,17] the hydroalkoxylation adducts from internal ynamides represent more interesting substrates due to their higher stability. Nevertheless, it would be better to obtain them as single isomer. Therefore, we decided to further investigate the addition of 1,3-diones to internal ynamides with the primary objective of developing a highly selective catalytic system promoting this reaction.

Results and Discussion

We started to survey various catalytic systems using as benchmark substrates methyl-substituted ynamide **1a** and dimedone **2a** (Table 1). In the absence of catalyst, the reaction required a heating at 80 °C in dichoroethane (DCE) to observe

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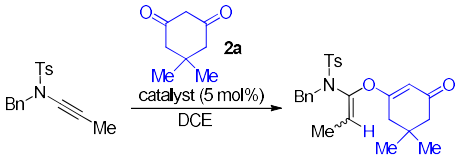
the adduct formation (entries 1 and 2). Despite a good *E*/*Z* ratio (19:1), the reaction required a prolonged heating time to reach a moderate yield. The use of the Herrmann-Beller catalyst (**H-B cat**) allowed the decrease of the reaction temperature, but only poor *E*/*Z* selectivities were observed (entries 3 and 4). With the gold complex [Au(PPh$_3$)NTf$_2$], the addition proceeded at lower temperature (40 °C, entry 5) but despite a long reaction time (16 h), the yield of **3aa** was disappointing (45%). At higher temperature, the gold catalyst showed a better efficiency but in detriment of the *E*/*Z* selectivity (entry 6).[18] Alternatively, we investigated several Lewis acids in order to efficiently activate the ynamide or/and the 1,3-dione.[19] In(OTf)$_3$ and Sn(OTf)$_2$ were found very active with a complete conversion in 1 h at 25 °C but low selectivities were obtained (entries 7 and 8). Copper(I) or (II) triflate slightly increased the *E*/*Z* selectivity (around 10:1, entries 9 and 10). Whereas Zn(OTf)$_2$ gave only a moderate selectivity (5.8:1, entry 11), ZnCl$_2$ or ZnBr$_2$ both allowed a substantial increase of the *E*/*Z* selectivity (around 25:1, entries 12 and 13) with a comparable efficiency. Finally, in presence of zinc(II) iodide, we were able to successfully achieve the addition at 25 °C in 1 h to give rise to exclusively *E*-adduct **3aa** (*E*/*Z* > 50:1) in 77% yield (entry 14). Concerning the difference of selectivies observed as a function of the zinc salt used, we assume that the halide or pseudohalide dissociation is favored in the case of ZnI$_2$ and might lead to the formation of chelate intermediates with reaction partners that trigger the exclusive *syn* addition of 1,3-dione **2a**.

Table 1. Optimization of the reaction conditions[a] [20]



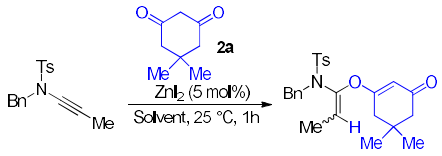
1a **3aa**

Entry	Catalyst	T (°C)	Time (h)	Yield (%)	*E*/*Z*[b]
1	None	60	5	NR	-
2	None	80	16	61	19:1
3	**H-B cat**	60	5	45	2:1
4	**H-B cat**	80	5	66	2:1
5	[Au(PPh$_3$)NTf$_2$]	40	16	45	19:1
6	[Au(PPh$_3$)NTf$_2$]	60	5	58	0.8:1
7	In(OTf)$_3$	25	1	90	2.8:1
8	Sn(OTf)$_2$	25	1	65	5.7:1
9	Cu(OTf)$_2$	25	1	92	10.4:1
10	Cu(OTf)·C$_6$H$_6$	25	1	91	11.6:1
11	Zn(OTf)$_2$	25	1	80	5.8:1
12	ZnCl$_2$	25	1	73	25:1
13	ZnBr$_2$	25	1	68	27:1
14	**ZnI$_2$**	**25**	**1**	**77**	**>50:1**

[a] Reaction conditions: ynamide **1a** (150 mg, 0.5 mmol), dimedone **2a** (70 mg, 0.5 mmol, 1 equiv.), catalyst (5 mol%; 2.5 mol% for dimeric **H-B cat**), DCE (3 mL, 0.17 M). [b] Determined by ^{1}H NMR. NR = No reaction.

The influence of the solvent was then investigated (Table 2). The reaction performed well in DCE, dichloromethane (DCM) and toluene with a complete selectivity in favor of the *E* adduct (entries 1-3). The use of moderately coordinating solvents such as THF or dioxane led to a slight decrease of both reaction yields and selectivities (entries 4 and 5). With the strongly acetonitrile, the drop of the selectivity was even more drastic (entry 6). No reaction occurred in DMF in spite of a prolonged reaction time (5 h, entry 7). These results, both in terms of efficiency and also selectivity, support the assumption of an ynamide activation by ZnI$_2$ and the formation of chelates with the reactants. Despite lower yield and *E*/*Z* ratio, the catalytic system was found compatible with MeOH and no product resulting from the competitive addition of MeOH was detected (entry 8).

Table 2. Solvent screening in ZnI$_2$-catalyzed addition of dimedone **2a** to ynamide **1a**[a]

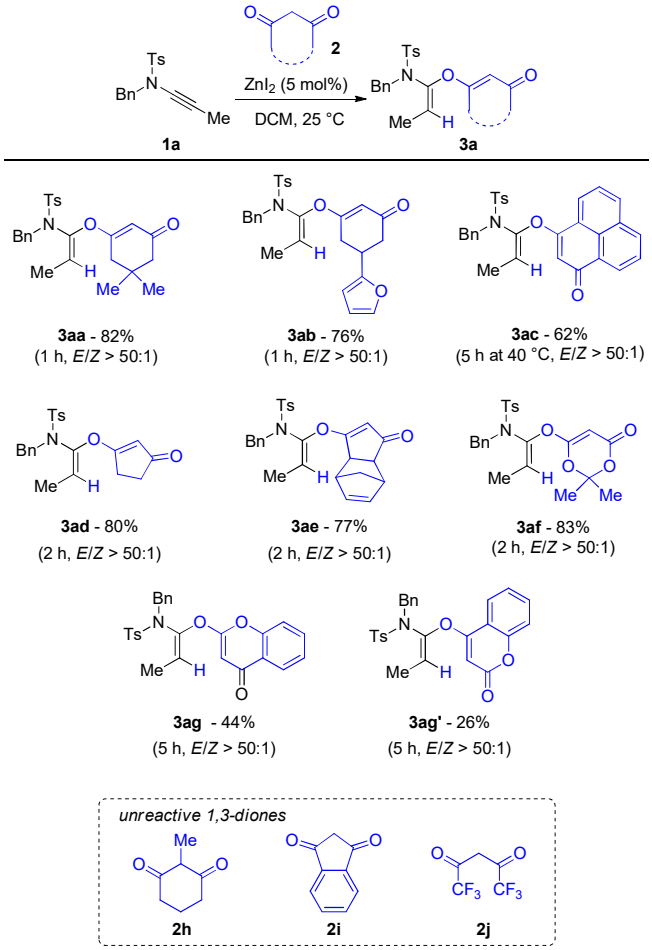


1a **3aa**

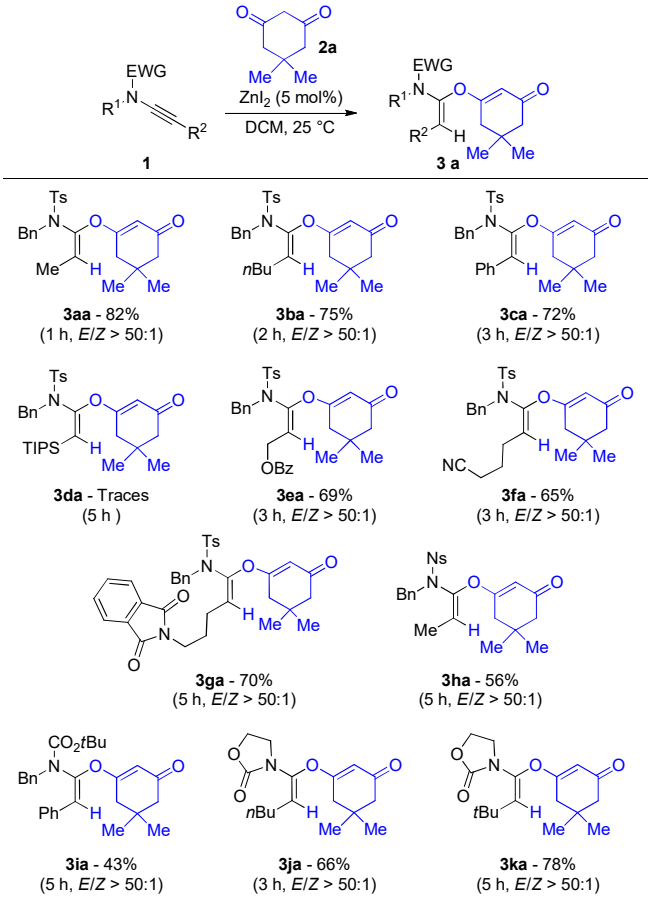
Entry	Solvent	Yield (%)	*E*/*Z*[b]
1	DCE	77	>50:1
2	**DCM**	**82**	**>50:1**
3	Toluene	72	>50:1
4	THF	58	33:1
5	1,4-Dioxane	57	31:1
6	MeCN	54	9.3:1
7[c]	DMF	NR	-
8	MeOH	49	24:1

[a] Reaction conditions: ynamide **1a** (150 mg, 0.5 mmol), dimedone **2a** (70 mg, 0.5 mmol, 1 equiv.), ZnI$_2$ (8 mg, 0.025 mmol, 5 mol%), solvent (3 mL, 0.17 M), 25 °C, 1 h. [b] Determined by ^{1}H NMR. [c] 5 h of reaction. NR = No reaction.

Having established the optimal reaction conditions, we further investigated the scope of the hydroalkoxylation with a range of 1,3-diones (Scheme 2). Similarly to dimedone **2a**, the furyl derivate **2b** gave rise rapidly to the *E* isomer of adduct **3ab** in a good yield. Owing to the poor solubility of the phenalene-1,3-dione **2c** at room temperature, the reaction mixture was heated at 40 °C for 5 h to reach a satisfactory yield of **3ac**. 2-Substitued 1,3-diones such **2h** did not react despite an increase of reaction temperature to 40 °C. Cyclopentane-1,3-dione based substrates **2d** and **2e** were good candidates affording the expected adducts in good yields and as *E* isomers only. Unfortunately, indanedione **2i** afforded a complex mixture of products. The ZnI$_2$-catalyzed addition was also efficiently achieved with Meldrum acid **2f** or 4-hydroxycoumarine **2g**. With **2g**, we obtained a separable mixture of compounds **3ag** and **3ag'** in a 1.7:1 ratio resulting from the competitive addition of the two nucleophilic oxygen atoms. The main limitation of this transformation remained that only cyclic 1,3-diones can be used.



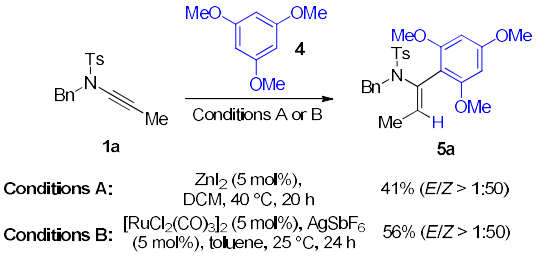
Scheme 2. Scope investigation of the ZnI_2-catalyzed addition with various 1,3-diones.



Scheme 3. Scope investigation with various internal ynamides (Ns = SO_2(*p*-NO_2-C_6H_4)).

Results depicted in Scheme 3 showed that broad structural variations of the ynamide partner can be accommodated. Except in the case of the triisopropylsilyl-subsituted ynamide **1d**, the nature of the ynamide substituent did not influenced the efficiency or selectivity outcomes of the additions. Corresponding adducts were isolated as *E*-isomers only. These included functionalized ynamides such as **1e**, **1f** and **1g** containing ester, nitrile and phtalimide groups respectively. For ynamides **1h** and **1i** bearing nosyl and Boc (*tert*-butyloxycarbonyl) as electron withdrawing group respectively, 5 h of reaction were necessary to obtain moderate isolated yields but the addition remained exclusively *syn*. Oxazolidinone-substituted ynamides **1j** and **1k** were also found compatible with the reaction conditions and the corresponding *E* adducts were isolated in moderate to good yields (66% and 78%, respectively). Hydroalkoxylation of ynamide **1k** bearing a bulky group (*t*Bu) indicated that the absence of reactivity of **1d** was probably due to electronic effects rather than a steric congestion.

Finally, we explored the possibility to expand this reaction to other nucleophiles. With the several catalytic systems investigated, phenols were found unreactive. As nitrogen, nucleophiles have already been well studied,[21] we focused on carbon nucleophiles. To the best of our knowledge intermolecular[22] hydroarylation of ynamides had only been reported with indole derivatives.[23] Therefore, we decided to test the hydroarylation with electron-rich trimethoxybenzene **4**. To our delight, the expected adduct **5a** was obtained with 41% yield as a single *Z*-isomer after 20 h of reaction at 40 °C (Scheme 4, condition A). Alternatively, it was also found that $[RuCl_2(CO)_3]_2$ in association with a silver salt (condition B)[24] performed better, since no thermal activation was required. In this case, **5a** was equally isolated as a single isomer. This transformation is interesting, not only because it represents a straightforward access to hindered and functionalized styrene derivatives but also



Scheme 4. Hydroarylation of ynamides.

because it indicates clearly that the role of the ZnI_2 catalyst is the activation of the ynamide partner.

Conclusions

In summary, among different catalytic systems tested, including transition metal-based catalysts and Lewis acids, we found that ZnI_2 was able to efficiently catalyze the *syn* hydroalkoxylation of internal ynamides with 1,3-diones. Advantageously, this transformation could be performed in various solvents. In a general manner, reactions proceeded smoothly at room temperature giving the adducts in good yields and as *E*-isomers exclusively. As shown by the scope investigation, various functional groups either on the ynamides or the 1,3-diones were well tolerated. This transformation was successfully transposed to the hydroarylation of ynamide with an electron-rich arene. This result seems to indicate that ZnI_2 activates the ynamides to trigger the hydroalkoxylation. Further studies on the reaction mechanism and the reactivity of adducts are currently undergoing in our laboratory.

Experimental Section

General procedure for the addition of 1,3-diones to terminal ynamides: In a 5 mL Schlenk flask under nitrogen were added in turn ZnI2 (8.0 mg, 0.0125 mmol, 5 mol%), the ynamide (0.5 mmol, 1 equiv.), 1,3-diketone derivatives (0.5 mmol, 1 equiv.) and DCM (3 mL). The reaction mixture was allowed to stir at 25 or 40 °C for the indicated reaction time. Volatiles were removed under reduced pressure and the crude residue was purified by silica gel flash chromatography using petroleum ether and ethyl acetate as eluent to give the pure desired product.

Acknowledgements ((optional))

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Keywords: Hydroalkoxylation • Ynamide • 1,3-Dione • Lewis acid • Enamine

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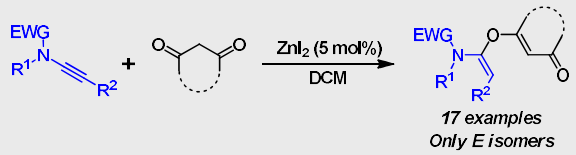

Ynamides*

*Rémi Plamont, Lionel. V. Graux, Hervé Clavier**

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Highly selective *syn* addition of 1,3-diones to internal ynamides catalyzed by zinc iodide

The hydroalkoxylation of internal ynamides with 1,3-diones was achieved in a highly *syn* manner using zinc iodide as Lewis acid catalyst. The scope of this transformation was found broad and compatible with various functional groups.

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