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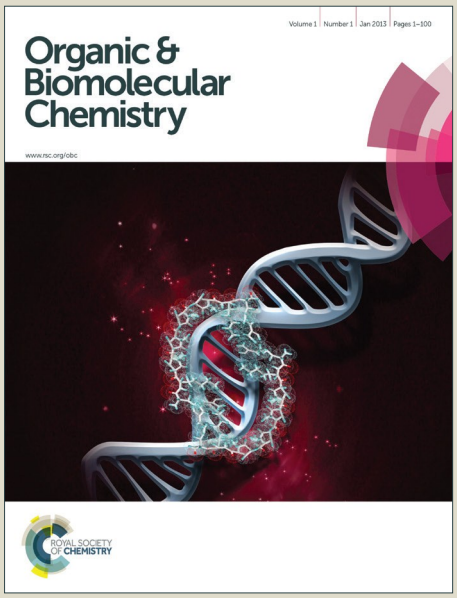

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Barluenga's Reagent with HBF_4 as An Efficient Catalyst for Alkyne-Carbonyl Metathesis of Unactivated Alkynes

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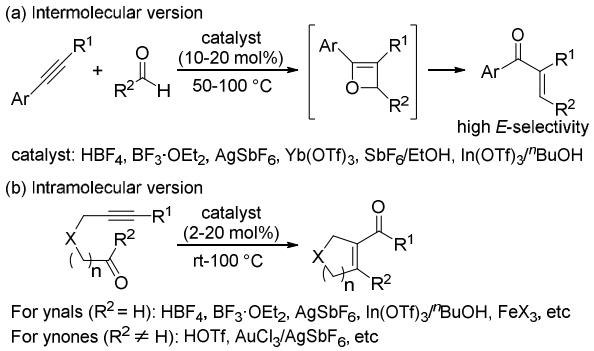
Barluenga's reagent (IPy_2BF_4, Py = pyridine) treated with HBF_4 efficiently catalyzes inter- and intramolecular alkyne-carbonyl metathesis of unactivated alkynes with aldehydes or ketones, most of which proceed at room temperature. This work represents the first catalytic application of the Barluenga's reagent.

Introduction

The Lewis or Brønsted acid-mediated oxygen transfer of a carbonyl group to a carbon–carbon triple bond, so-called alkyne-carbonyl metathesis, leads to the stereoselective formation of α,β-unsaturated carbonyl compounds (Scheme 1),[1] which are not only useful building blocks in organic syntheses but also a significant motif in natural products and biologically active compounds.[2] This reaction is suggested to proceed via a [2+2] cycloadduct intermediate[3] by ab initio calculations and some experimental evidence.[4] Since Krische's[5] and Yamamoto's reports,[6] the catalytic alkyne-carbonyl metathesis of unactivated alkynes has gathered attention as an efficient and atom-economical manner alternative to the Wittig reaction, and thus π- or σ-electrophilic Lewis acids,[5,6,7] the combination of Lewis acids with alcohols,[8] and Brønsted acids[5,9,10] have been reported to act as the catalyst (Scheme 1). Recently, these methods have been applied to the construction of various heterocyclic frameworks[11] or natural products,[12] and to domino reactions.[6b,8a,13] However, these reactions, particularly intermolecular reactions,[5,8] require the thermal conditions (50 to 100 ºC). As part of our researches on the catalytic alkyne-carbonyl metathesis,[8a,13a,b] we herein report the present reaction at room temperature by iodine(I)-catalyst.



Scheme 1. Catalytic alkyne-carbonyl metathesis of unactivated alkynes.

Bis(pyridine)iodonium(I) tetrafluoroborate (IPy_2BF_4) has been developed by Barluenga, and later has been employed as a iodonium source and oxidant.[14] In particular, the utility of Barluenga's reagent has been widely demonstrated in iodination of alkenes, alkynes and aromatics,[14,15] which involves more active iodonium species *in situ* generated from Barluenga's reagent and acid additive than general iodine(I) reagents such as molecular iodine and *N*-iodosuccinimide (NIS). Furthermore, the iodonium species has been known to work well as a σ-electrophilic Lewis acid for carbonyl groups in the oxidative arylation of aldehydes.[16] Also, NIS/acid systems has been showed their efficiency as a superelectrophilic iodine(I) species not only in iodination of aromatics,[17a-c] but also in the activation of glycosides.[17d-f] However, although molecular iodine[18] and organoiodine compounds (such as iodoperfluoroalkane or –arene and 2-iodoimidazolium salts)[19] have been utilized in the catalytic activation of carbonyl oxygen and sp^2-hybridized nitrogen atoms, the catalytic application of these iodine(I) species has been unknown. Therefore, we focused on the new possibility of these iodine(I) species as a σ- and/or π-acid catalyst for the catalytic alkyne-carbonyl metathesis.

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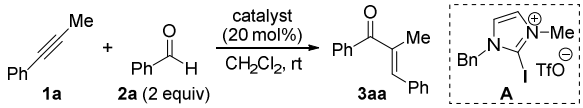
Results and Discussion

Initially, the screening of various iodine(I) catalysts (20 mol%) was examined for the metathesis of alkyne **1a** and aldehyde **2a** (2 equiv) in CH_2Cl_2 (Table 1). Molecular iodine, NIS and 2-iodoimidazolium salt **A** did not catalyzed the present reaction at room temperature (entries 1-3), while NIS activated by HBF_4 and IPy_2BF_4 pretreated with HBF_4 (2 equiv to IPy_2BF_4) led to the formation of the desired product **3aa** (entries 4 and 5). Particularly, by the use of the IPy_2BF_4/2 HBF_4 catalytic system, **3aa** was obtained in 70% yield within only 1 h (entry 5). Since the use of IPy_2BF_4 or pyridinium tetrafluoroborate ($PyHBF_4$), which is a side product formed by treatment of IPy_2BF_4 with HBF_4, did not afford **3aa** (entries 6 and 7), these reagents would not be involved in IPy_2BF_4/2 HBF_4 catalytic system. It should be mentioned that IPy_2BF_4/2 HBF_4 catalytic system was more effective on the present reaction than the widely used catalysts such as HBF_4,[5,10,13c] trifluoromethanesulfonic acid (TfOH)[9a,b,13d,h-j] and $BF_3{\cdot}Et_2O$[3a,b,d-g,5,11a] (entry 5 vs entries 8-11).

Table 1. Screening of catalysts.

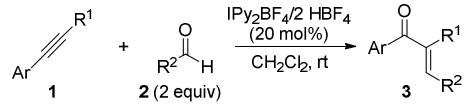


entry	catalyst	time/h	**3aa**/%[a]
1	I_2	20	0
2	NIS	20	0
3	**A**	20	0
4	NIS/HBF_4[b]	1	47
5	IPy_2BF_4/2 HBF_4[b]	1	70[c]
6	IPy_2BF_4	20	0
7	$PyHBF_4$	20	0
8	HBF_4[b]	10	55
9	HBF_4[b,d]	1	60
10	HOTf	20	53
11	$BF_3{\cdot}Et_2O$	20	27

[a] Values were determined by ^{1}H NMR analysis using DCE as an internal standard. [b] $HBF_4{\cdot}Et_2O$ was employed. [c] Isolated yield. [d] 40 mol%.

Next, the scope of the intramolecular alkyne-carbonyl metathesis catalyzed by IPy_2BF_4/2 HBF_4 system (20 mol%) was investigated at room temperature and the results were summarized in Table 2. Both internal and terminal aromatic alkynes **1a** and **1b** smoothly reacted not only with aromatic aldehydes **2a-c** but also with aliphatic aldehydes **2e-g** to give corresponding α,β-enones **3** in 52-73% yields (entries 1-3 and 5-12), albeit low yield in the case of electron-rich aldehyde even at 90 ºC for 20 h in DCE (1,2-dichloroethane, entry 4). It should be noteworthy that most case of these substrates proceeded at room temperature, because these reactions require higher temperature [HBF_4: 50-80 ºC in DCE, $In(OTf)_3$-BuOH: 100 ºC][5,8] and some cases of aliphatic aldehydes did not afforded the corresponding products.[8b] The present catalytic systems could be applied to the alkyne-carbonyl metathesis of aromatic alkynes **1c-f**, regardless of the electron-rich or electron-deficient nature of the substituents on the aromatic rings (entries 13-16), and **1g** having other alkyl substituent at the alkyne terminus (entry 17).

Table 2. Substrate scope for intermolecular reactions.



1a: Ar = Ph, R^1 = Me
1b: Ar = Ph, R^1 = H
1c: Ar = 4-MeC_6H_4, R^1 = H
1d: Ar = 4-$MeOC_6H_4$, R^1 = H
1e: Ar = 4-ClC_6H_4, R^1 = H
1f : Ar = 4-$CF_3C_6H_4$, R^1 = H
1g: Ar = Ph, R^1 = ^{n}Bu

entry	**1**	**2**	R^2	time/h	**3**/%[a]	
1	**1a**	**2a**	Ph	1	**3aa**	70
2	**1a**	**2b**	4-$NO_2C_6H_4$	3	**3ab**	64
3	**1a**	**2c**	4-BrC_6H_4	1	**3ac**	66
4[b]	**1a**	**2d**	2-thienyl	20	**3ad**	18
5	**1a**	**2e**	^{i}PrCH$_2$	3	**3ae**	73
6	**1a**	**2f**	^{i}Pr	20	**3af**	72
7	**1a**	**2g**	^{t}Bu	20	**3ag**	58
8	**1b**	**2a**	Ph	20	**3ba**	63
9	**1b**	**2c**	4-BrC_6H_4	20	**3bc**	55
10	**1b**	**2e**	^{i}PrCH$_2$	20	**3be**	63
11	**1b**	**2f**	^{i}Pr	20	**3bf**	64
12	**1b**	**2g**	^{t}Bu	20	**3bg**	52
13	**1c**	**2a**	Ph	20	**3ca**	55
14	**1d**	**2a**	Ph	20	**3da**	44
15	**1e**	**2a**	Ph	20	**3ea**	63
16	**1f**	**2a**	Ph	20	**3fa**	78
17	**1g**	**2a**	Ph	3	**3ga**	40

[a] Isolated yield. [b] Reaction temperature: 90 ºC, solvent: DCE.

Furthermore, the present catalytic metathesis could be extended to the intramolecular reactions of ynals and ynone (Scheme 2). Thus, IPy_2BF_4/2 HBF_4 systems (20 mol%) brought about the conversion of ynals **4a-c** and **6b** to the 5- and 6-membered cyclic enones **5a-c** and **7b** in 31-72% yields, although NIS/HBF_4 systems showed superior results in reactions of the 1,6-ynals (**5a**: 80%, **5b**: 40%).[20] Even by the use of 5 mol% IPy_2BF_4/2 HBF_4 systems, 1,7-ynal **6a** and 1,7-ynone **6c** afforded the corresponding cyclic enones **7a** and **7c** in 80% and 60% yields, respectively. Notably, in contrast to the previous methods (HBF_4: 50 ºC in DCE, $FeCl_3$: refluxing in DCE),[5,11b,d] the reactions of less reactive aliphatic ynals **4b**, **6b** and ynone **6c** smoothly proceeded at room temperature as well as aromatic ynals, although 1,8-ynal **6d** required higher temperature (90 ºC in DCE).

To gain a qualitative understanding of the activation of alkynes and/or aldehydes by the present catalytic systems, we carried out NMR studies using 1:1 mixture of alkyne **1a** and benzaldehyde (**2a**) with various additives in CD_2Cl_2 at -78 ºC (Table 3, see also Supporting Information). The ^{13}C NMR spectrum (125 MHz) in the presence of $PyHBF_4$ (1 equiv)

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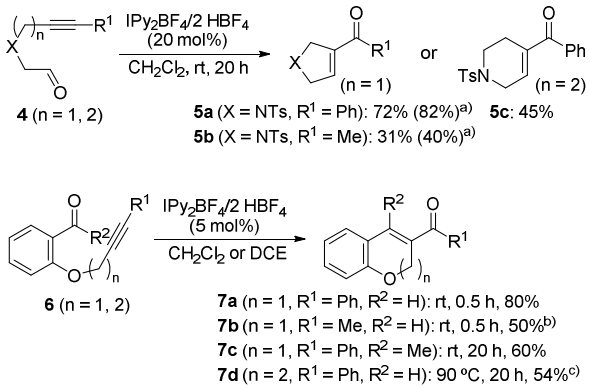
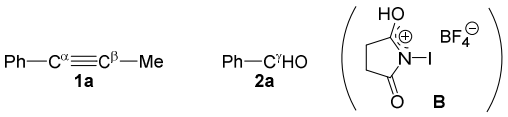
showed slight upfield shifts of the sp-carbons (C^{α} and C^{β}, $\Delta\delta$ = -0.13 and -0.07) of **1a** and the carbonyl-carbon (C^{γ}, $\Delta\delta$ = -0.02) of **2a** compared with that in the absence of any additives (entry 1). On the other hand, the addition of $BF_3{\cdot}Et_2O$, HBF_4, NIS/HBF_4, or IPy_2BF_4/2 HBF_4 (0.5 equiv each)[21] instead of $PyHBF_4$ led to the significant downfield shift of C^{γ} (entries 2-5, $\Delta\delta$ = 0.22–1.90), and the case of IPy_2BF_4/2 HBF_4 was particularly notable (entry 5, $\Delta\delta$ = 1.90). These results suggest that an iodonium species such as IBF_4 and/or IF generated from IPy_2BF_4 and HBF_4 serve as a σ-acid for the activation of the aldehyde. Barluenga *et al*. proposed the involvement of the similar iodonium species in the oxidative arylation of aldehydes.[16] Furthermore, the present iodonium species was found out to have the stronger σ-acidity than HBF_4 and an iodine species **B** derived from NIS and HBF_4. Since the iodine species such as **B** was observed in a ^{13}C NMR spectrum of a mixture of NIS and an acid by Olah et al., **B** was considered to be involved in the present reaction.



a) Values in the parenthesis show yields in cases of NIS/HBF_4 (20 mol%) as a catalyst. b) Catalyst: 15 mol%. c) Catalyst: 20 mol%.

Scheme 2. Substrate scope for intramolecular reactions.

Table 3. ^{13}C NMR experiments using **1a** and **2a**.[a)]



entry	additive (equiv)	$\Delta\delta^{b)}$		
		C^{α}	C^{β}	C^{γ}
1	$PyHBF_4$ (1)	-0.13	-0.07	-0.02
2	$BF_3{\cdot}Et_2O$ (0.5)	-0.03	-0.02	0.22
3	HBF_4[c)] (0.5)	-0.01	-0.02	0.73
4	NIS/HBF_4[c)] (0.5)	0.00	-0.01	0.77
5	IPy_2BF_4/2 HBF_4[c)] (0.5)	-0.02	0.00	1.90

[a)] ^{13}C NMR spectra (125 MHz) of a 1:1 mixture of **1a** and **2a** in the presence of various additives (0.5 or 1equiv) were measured in CD_2Cl_2 at -78 °C. [b)] Differences between chemical shifts in the presence and absence of additive. Negative values showed the shift to a higher field. [c)] $HBF_4{\cdot}Et_2O$ was employed.

Conclusions

In conclusion, we have developed the catalytic inter- and intramolecular alkyne-carbonyl metathesis of unactivated alkynes with aldehydes or ketones by IPy_2BF_4/2 HBF_4 system (5-20 mol%), which mostly proceed at room temperature. Furthermore, the present catalytic system was demonstrated to have the stronger σ-acidity than the widely used catalysts by NMR experiments. Further investigations will focus on the mechanism studies and extending this strategy to domino reactions based on the alkyne-carbonyl metathesis.

Acknowledgements

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21 Since the use of 1 equiv HBF_4, NIS/HBF_4, or IPy_2BF_4/2 HBF_4 brought about complex mixtures even at -78 ºC, the chemical shifts of **1a** and **2a** could not be observed properly.

