



Cobalt Catalysis

Cobalt-Catalysed C–C Bond Formation and [2+2+2] Annulation of 1,3-Dicarbonyls to Terminal Alkynes

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Abstract: A highly regioselective $[Cp*Co(CO)I_2]$ -catalyzed addition of 1,3-diketones to terminal alkynes at room temperature has been achieved using $Cu(OTf)_2$ as a co-catalyst. The reaction of 1,3-diketones substituted at active methylene carbon with phenyl acetylenes having an electron-withdrawing group or a

bulky group results in the formation of the 2-alkenylated 1,3dicarbonyl product, but phenyl acetylenes with electron donating group led to the formation of tetrahydronaphthalene and terphenyl.

Introduction

The carbon–carbon (C–C) bond formation reaction remains one of the most useful and fundamental reactions in the development of organic chemistry. Intramolecular addition of activated carbonyl compounds, enolates or enols to an unsaturated enophile, leading to cyclization, with 100 % atom economy, is popularly known as Conia-Ene reaction.^[11] The classic transformation involves thermal cyclization, ^[1a,2] however chemists have developed catalytic, especially transition metal catalyzed cyclization procedures, which were well documented in the literature.^[1b,1c,3–5]

A relatively new intermolecular method of the Conia-Ene reaction for C–C bond formation, involving the reaction of 1,3diketone and unactivated terminal alkynes, has gained importance in recent years.^[6] In the pioneering work, Nakamura and co-workers^[6] reported the first example for C–C bond formation from 1,3-diketones and terminal alkynes in the presence of In(OTf)₃, as a catalyst, at very high temperature (up to 140 °C). Subsequently, this reaction was reported to be catalyzed by Re^{1,[7]} In^{III},^[6,8] Ru,^[9] Ir^[10] and Au¹/Ga^{III}.^[11] However, these transformations require two to five equivalents of an alkyne, high temperature, costly metal catalyst, and longer reaction time.

Malacria and co-workers explored Co^I-catalyzed intramolecular cycloisomerization through Conia-Ene reaction in high yields with moderate to total control of stereoselectivity.^[4] In contrast Co^{III}-catalyzed intramolecular cycloisomerization or intermolecular reaction of 1,3-diketone and unactivated terminal alkynes has not been reported till date to the best of our knowledge. In recent years, an air-stable Co^{III} catalyst [Cp*Co(CO)I₂], which can be easily synthesized,^[12] emerged as a robust, highly efficient and cheaper catalyst for the construction of C–C bonds.^[13]

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Results and Discussion

In continuation of our work to develop alternative catalytic approaches,^[14] we report herein a simple, eco-friendly, cost effective and time efficient synthesis of 2-alkenylated 1,3-dicarbonyl and [2+2+2] cycloaddition reaction product. Initially, diketone **1a** (1.0 mmol) and terminal alkyne **2a** (1.2 mmol) were stirred in the presence of 5 mol-% each of Co^{III} and Cu(OTf)₂ catalyst in dichloroethane (DCE) at room temperature. To our delight, this reaction leads to the formation of 2-alkenylated 1,3-dicarbonyl product **3a** as confirmed by NMR spectroscopy and Mass spectrometry (Scheme 1).



Scheme 1. Synthesis of 3-(1-phenylvinyl)pentane-2,4-dione 3a.

To optimize the reaction condition acetylacetone 1a and phenylacetylene 2a were taken as model substrate. The effects of different catalysts, co-catalysts, solvent, and temperature were examined on the model substrates, the results are summarized in Table 1. Initially, a mixture of 1a (1.0 mmol) and 2a (1.2 mmol) in DCE (1.0 mL) in the presence of Co^{III} and Cu(OTf)₂ catalyst (5 mol-% of each) were stirred at room temperature (r.t.). The desired product 3a was isolated in 70 % yield and the reaction was completed in 2.5 h (Table 1, entry 1). However, in the absence of Cu(OTf)₂ only a trace amount of the desired product 3a was obtained even after 24 h of stirring and most of the starting substrates were isolated (Table 1, entry 2). It is important to mention here that no product formation was noticed when the reaction was carried out using only $Cu(OTf)_2$ as a catalyst, which is well in agreement with the earlier observation that Cu(OTf)₂ itself does not catalyze this reaction.^[8a] This confirms that Cu(OTf)₂ may act as a co-catalyst in this reaction. Triflates of Sc^{III}, Ni^{II} and Ag^I were also examined but they failed to enhance the product yield (Table 1, entries 3 & 5). To check the effect of other counter anions AgSbF₆ (Table 1, entry 6),





Cu(OAc)₂, CuBr₂ and CuI have been used instead of Cu(OTf)₂. Except for $AgSbF_6$ (Table 1, entry 6), others were failed to yield even trace of the product. Other catalysts, in combination with Cu(OTf)₂ were not able to enhance the yield of the reaction (Table 1, entries 7-11). In order to explore the role of the solvent, the reaction was carried out in DCM, THF, MeOH, ACN, DMF, and *n*-Hexane but no improvement was observed (Table 1, entries 12-17). Interestingly, under neat condition maximum yield (92 %) of the desired product was obtained in a very short time i.e. within 30 minutes (Table 1, entry 18). Finally, the effect of temperature was studied, and it was observed that increasing or decreasing the temperature has a negative impact on the outcome of the reaction (Table 1, entries 19–21). Variation in the percentage of Co^{III} catalyst or $Cu(OTf)_2$ also does not have any positive effect on the reaction. Thus, 5 mol-% of Co^{III} catalyst, 5 mol-% of Cu(OTf)₂ as co-catalyst, under neat condition at room temperature was found to be optimum reaction conditions for the synthesis of 3a from 1a (1 mmol) and 2a (1.2 mmol) (Table 1, entry 18).

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

				OH Ö		
	0 0	H H	conditio	ns Me		Ме
M	e Me		-			
	1a	2a			3a	
Entry	Catalyst (5 mol-%)	Additive (5 mol-%)	Solvent	Temp. [°C]	Time	Yield ^[b] [%]
1	Co ^{III}	Cu(OTf) ₂	DCE	r.t.	2.5 h	70
2	Co ^{III}	-	DCE	r.t.	24 h	trace
3	Co ^{III}	Sc(OTf) ₃	DCE	r.t.	2.5 h	62
4	Co ^{III}	Ni(OTf) ₂	DCE	r.t.	6 h	54
5	Co ^{III}	AgOTf	DCE	r.t.	12 h	60
6	Co ^{III}	AgSbF ₆	DCE	r.t.	1 h	65
7	CoBr ₂	Cu(OTf) ₂	DCE	r.t.	24 h	_[c]
8	[Co(NH ₃) ₆]Cl ₃	Cu(OTf) ₂	DCE	r.t.	24 h	_[c]
9	FeCl₃	Cu(OTf) ₂	DCE	r.t.	24 h	_[c]
10	NiCl ₂ •6H ₂ O	Cu(OTf) ₂	DCE	r.t.	24 h	_[c]
11	CoCl ₂ •6H ₂ O	Cu(OTf) ₂	DCE	r.t.	24 h	trace
12	Co ^{III}	Cu(OTf) ₂	DCM	r.t.	2.5 h	75
13	Co ^{III}	Cu(OTf) ₂	THF	r.t.	2.5 h	50
14	Co ^{III}	Cu(OTf) ₂	MeOH	r.t.	2.5 h	47
15	Co ^{III}	Cu(OTf) ₂	ACN	r.t.	2.5 h	58
16	Co ^{III}	Cu(OTf) ₂	DMF	r.t.	2.5 h	41
17	Co ^{III}	Cu(OTf) ₂	Hexane	r.t.	2.5 h	66
18	Co ^{III}	Cu(OTf) ₂	none	r.t.	30 min	92
19	Co ^{III}	Cu(OTf) ₂	none	40	30 min	80
20	Co ^{III}	Cu(OTf) ₂	none	50	30 min	79
21	Co ^{III}	Cu(OTf) ₂	none	20	40 min	75

[a] Reaction Conditions: **1a** (1.0 mmol) and **2a** (1.2 mmol) in described solvent (1.0 mL), catalyst, additive and temperature. [b] Isolated yield. [c] No desired product formation.

With the optimized reaction conditions in hand, we evaluated the substrate scope and generality of the reaction, the results are summarized in Table 2. A variety of terminal alkynes with acetylacetone have been studied. All the reactions proceeded smoothly. Phenylacetylenes, substituted with electrondonating or -withdrawing groups at *para*-position, yielded products in 80–92 % yields (Table 2, entries 1–6). Aliphatic alkynes were found to be less reactive in this reaction and the products obtained in 52–55 % yield (Table 2, entries 7–9). Phenyl-substituted propargyl ethers have also contributed well in this reaction and the corresponding products (**3j** & **3k**) were obtained in good yield (70–72 %) (Table 2, entries 10–11). Reaction with nitrogen-atom containing alkynes, like 4-*N*,*N*-dimeth-ylaminophenylacetylene (**2l**) and 2-ethynylpyridine (**2m**), did not proceed to the product formation with all the reactants remained unreacted even after stirring the reaction mixture for 24 hours (Table 2, entries 12 and 13). This may be attributed to the complex formation between nitrogen-containing alkynes and metal itself. However, reaction with 4-trifluoromethylphen-ylacetylene (**2n**), and cyclopropylacetylene (**2o**) led to the formation of a complex reaction mixture (Table 2, entries 14 & 15), with trace amounts of the desired product.

Table 2. Exploring alkyne scope with acetylacetone.^[a]

Me 1a	Cp*0 Me + RH 2	Co(CO)I ₂ (5 mol %) (OTf) ₂ (5 mol %) rt, 60 min, neat	Me Me
Entry	R	Product	Yield ^[b] [%]
1	C ₆ H ₅ (2a)	3a ^[6]	92
2	4-MeC ₆ H ₄ (2b)	3b ^[9a]	84
3	4-MeOC ₆ H ₄ (2c)	3c ^[9a]	81
4	4- <i>t</i> Bu-C ₆ H ₄ (2d)	3d ^[11]	80
5	4-BrC ₆ H ₄ (2e)	3e ^[9a]	87
6	4-FC ₆ H ₄ (2f)	3f ^[9a]	85
7	C ₃ H ₇ (2g)	3g	52
8	C ₄ H ₉ (2h)	3h	55
9	C ₅ H ₁₁ (2i)	3i ^[8b]	54
10	4-MeC ₆ H ₄ OCH ₂ (2j)	Зј	70
11	4-EtC ₆ H ₄ OCH ₂ (2k)	3k	72
12	4-Me ₂ NC ₆ H ₄ (2I)	31	_[c]
13	2-pyridyl (2m)	3m	_[c]
14	4-CF ₃ C ₆ H ₄ (2n)	3n	_[d,e]
15	<i>c</i> -propyl (20)	30	_[d,e]

[a] Reaction conditions: **2** (1.2 mmol) was added slowly to a mixture of **1** (1.0 mmol), Co^{III} (5 mol-%) and Cu(OTf)₂ (5 mol-%) in an oven-dried round-bottomed flask and stirred the mixture for 60 min (overnight in case of alkyne **2j** and **2k**). [b] Isolated yields. [c] No reaction. [d] Trace of product formation. [e] Complex reaction mixture.

To explore the structural viability of this protocol we switched from acetylacetone (**1a**) to 2-acetyl-cyclohexanone (**1b**), and 3-methyl-2,4-pentanae-dione (**1c**), which have substitution at active-methylene carbon. The reaction of 2-acetyl-cyclohexanone (**1b**), with alkynes **2a** and **2d**, lead to the desired products **3p** and **3q** in 78 % and 80 % yield respectively (Table 3, products **3p** and **3q**). However, the reaction of **1c** with **2b** and **2f** lead to the formation of products **3r** and **3s**).

Nakamura^[15] and Takai^[16] both have reported the transition metal catalyzed [2+2+2] cycloaddition of 1,3-diketone and terminal alkynes. Takai and co-workers have reported some different results when 1,3-diketone has a substituent on its active methylene moiety.^[17] To our surprise, in a few cases, we too have observed [2+2+2] deacylative cycloaddition reaction between **1b/1c** with terminal alkynes having –OMe or –Me (electron donating) group on the phenyl ring. Reaction of **1b** with **2c**, **2b** or *m*-MeOC₆H₄CCH (**2o**) gave tetrahydronaphthalene **4a**–





Table 3. Exploring scope of active methylene substituted 1,3-diketone with alkynes. $^{\left[a\right] }$



[a] Reaction Condition: **2** (0.6 mmol) was added slowly to the mixture of **1b** (**1c**) (0.5 mmol), Co^{III} catalyst (5 mol-%) and Cu(OTf)₂ (5 mol-%) in an ovendried round-bottomed flask and stirred the mixture for 60 min. [b] Cu(OTf)₂ (2 mol-%) was used. [c] In case of products **4**, **2** (1.2 mmol) was used.

4c in 57–61 % yield (Table 3). However, the reaction of **1c** with **2c** led to the formation of terphenyl **4d** in 58 % of yield (Table 3). Further, our efforts to explore the reaction of acetyl-acetone with internal alkyne and β -keto ester with terminal alkynes were not fruitful.

The structures of all the newly synthesized molecules **3** and **4** were deduced from their satisfactory spectral (IR, ¹H, ¹³C NMR and HRMS) studies, and established by the X-ray single crystal diffraction analysis of compounds **3p**, **4a**, and **4d** (Figure 1).



Figure 1. ORTEP diagram of **3p**, **4a**, and **4d**.^[18]

The regioselectivity may be explained by the plausible mechanism (Scheme 2) along with considering the previous reports.^[4,15b] It is supposed that, the iodide ligand of Co^{III} catalyst replaced by triflate to form **A**, which may form intermediate **B** with **1a** and **2** followed by removal of triflic acid (HOTf). Now, the nucleophilic carbon is close enough, to regioselectively attack the alkyne and form complex **C**, which may further yields desired product **3** and regenerate active catalyst **A** (Scheme 2a). If there is substitution at active methylene carbon center of 1,3diketone such as **1b** or **1c**, intermediate **C** can be written as C' (Scheme 2b). Under the influence of phenylacetylenes with electron donating group, it is possible that another alkyne approaches to metal centre of C' to form intermediate D, which undergoes C–C coupling followed by ring formation to yield E. The oxygen atom, bonded with metal, may attack carbonyl carbon, to form a 4-membered oxetane ring-containing intermediate F, which on aromatization followed by reaction with HOTf regenerates catalyst A and final product 4.



Scheme 2. Plausible mechanism for the synthesis of 3 & 4.

Conclusions

In conclusion, we have achieved the addition of 1,3-diketone to terminal alkynes catalyzed by Co^{III} catalyst and co-catalyzed by $Cu(OTf)_2$ under neat conditions at room temperature, leading to the regioselective synthesis of product **3**. 1,3-Diketones substituted at the active methylene carbon center give [2+2+2] cycloaddition reaction product in some cases.

Experimental Section

Representative Procedure for the Synthesis of 3: Alkyne **2** (1.20 mmol) was added slowly to a mixture of 1,3-diketone **1** (1.0 mmol), Co^{III} (5 mol-%) and Cu(OTf)₂ (5 mol-%) in an oven-dried round-bottomed flask and stirred the mixture for 60 min (overnight in case of alkyne **2j** and **2k**). The reaction mixture was directly purified by column chromatography using silica gel (100–200 Mesh) as stationary phase and *n*-hexane (100 %) or 1 % mixture of ethyl acetate in *n*-hexane as eluent.





Representative Procedure for the Synthesis of 4: Alkyne 2 (1.2 mmol) was added slowly to the mixture of 1,3-diketone **1b** (**1c**) (0.5 mmol), Co^{III} catalyst (5 mol-%) and Cu(OTf)₂ (5 mol-%) in an oven-dried round-bottomed flask and stirred the mixture for 60 min. The reaction mixture was directly purified by column chromatography using silica gel (100–200 Mesh) as stationary phase and *n*-hexane (100 %) or 1 % mixture of ethyl acetate in *n*-hexane as eluent.

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Keywords: Alkynes · Cobalt · Copper · Cyclization · Homogeneous catalysis · Ketones

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Cobalt-Catalysed C-C Bond Forma tion and [2+2+2] Annulation of 1,3 Dicarbonyls to Terminal Alkynes



A highly regioselective $[Cp*Co(CO)I_2]$ catalyzed addition of 1,3-diketones to terminal alkynes at room temperature have been achieved using Cu(OTf)₂ as co-catalyst. In some cases, the reaction of 1,3-diketones substituted at the active methylene carbon atom with electron donating groups gave tetrahydronaphthalene and terphenyl.

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