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A highly selective cobalt-catalyzed carbonylative cyclization of internal alkynes with carbon monoxide and organic thiols

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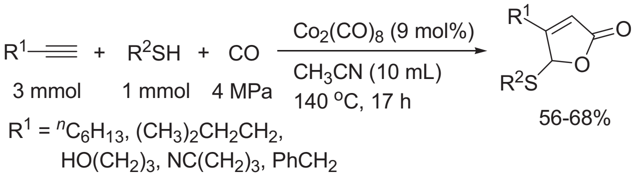
ABSTRACT

Despite the fact that many transition-metal-catalyzed reactions of organosulfur compounds with internal alkynes are ineffective, cobalt carbonyl ($Co_2(CO)_8$) is an excellent catalyst for carbonylative cyclization of internal alkynes with carbon monoxide. When $Co_2(CO)_8$-catalyzed reactions of internal alkynes with organic thiols are conducted in acetonitrile under 4 MPa pressure of carbon monoxide, thiolative lactonization of internal alkynes successfully takes place with incorporation of two molecules of CO. This carbonylation provides a useful tool to prepare the corresponding α,β-unsaturated γ-thio-γ-lactones (butenolide derivatives) in good yields. In the cases of unsymmetrical alkynes, such as 2-octyne and 6-methyl-2-heptyne, the thiolative lactonization proceeds with moderate regioselectivity to give the butenolide derivatives on which the carbonyl group preferentially bonds to the less hindered acetylenic carbon. Mechanistic pathways about the present thiolative lactonization are also discussed.

1. Introduction

Transition-metal-catalyzed carbonylation with simultaneous introduction of a heteroatom is one of the most important tools for synthesizing carbonyl compounds bearing heteroatom functional groups.[1] Organosilicon compounds, such as hydrosilanes have been employed frequently for this purpose.[2] Although organosulfur compounds are useful synthetic intermediates, only very limited examples of transition-metal-catalyzed carbonylation with concurrent introduction of sulfur functions have been reported previously.[3] Furthermore, examples of transition-metal-catalyzed addition of heteroatom compounds to internal alkynes are also very limited because steric hindrance by internal alkynes inhibits their coordination to catalysts.

Recently, we and other groups developed carbonylation of terminal alkynes with carbon monoxide and organosulfur compounds catalyzed by group 10 transition-metal complexes.[1g,k,3g,h,4] Moreover, we very recently found that cobalt carbonyl ($Co_2(CO)_8$) is an excellent catalyst for the thiolative double carbonylation of terminal alkynes with CO and organic thiols (Eq. 1).[5] This cobalt-catalyzed double carbonylation was applied to several terminal alkynes bearing branched alkyl group, hydroxyl group, cyano group, and benzyl group to give the corresponding butenolide derivatives with excellent regioselectivity. The structure of double carbonylation product was determined unambiguously by X-ray analysis.



(1)

Very recently, we have revealed the thiolative carbonylation of internal alkynes with CO and organic disulfides by using $Co_2(CO)_8$ as the catalyst (Eq. 2).[6] Notably, this carbonylation is of special interest as it is a rare example of the carbonylation of internal alkynes. The formation of stable cobalt–alkyne complexes probably contributes to the success of this reaction. Since sulfur compounds are generally believed to be catalyst poisons,[7] these catalytic reactions introduce a new field of transition-metal-catalyzed reactions of organosulfur compounds with internal alkynes.

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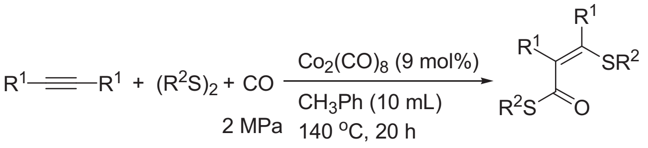
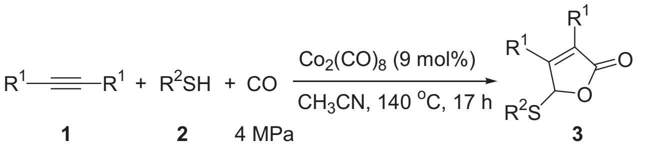


(2)

Herein, we report a novel $Co_2(CO)_8$-catalyzed thiolative carbonylation of internal alkynes **1** with organic thiols **2** and carbon monoxide. This reaction affords α,β-unsaturated γ-thio-γ-lactone derivatives **3** (butenolide derivatives) in good yields (Eq. 3).

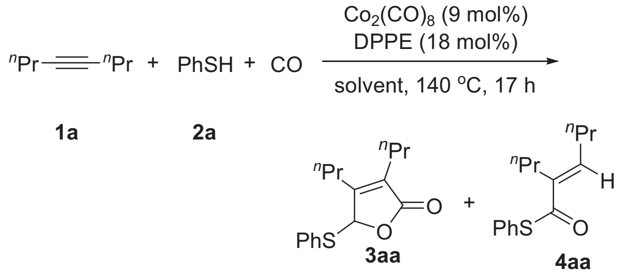


(3)

2. Results and discussion

When the reaction of 4-octyne (**1a**, 3 mmol) with benzenethiol (**2a**, 1 mmol) was conducted in acetonitrile (5 mL) under 2 MPa CO in the presence of 9 mol% dicobalt octacarbonyl and 18 mol% 1,2-bis(diphenylphosphino)ethane (DPPE), α,β-unsaturated γ-phenylthio-γ-lactone (**3aa**) and α,β-unsaturated thioester (**4aa**) were obtained in 36% and 7% yields, respectively (Table 1, Entry 1).

Table 1
Cobalt-catalyzed double carbonylation of 4-octyne[a]



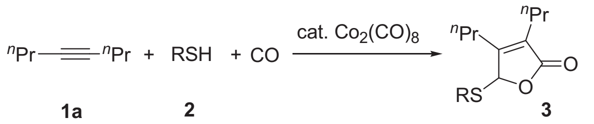
Entry	CO (MPa)	CH_3CN (mL)	Yield (%)[b]	
			3aa	**4aa**
1	2	5	36	7
2	2	10	48	10
3	2	15	52	4
4	1	10	37	6
5	3	10	63	5
6	4	10	56	5
7[c]	3	10	57	15
8[c]	4	10	70 (73)	12 (4)

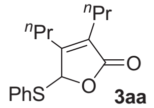
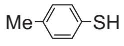
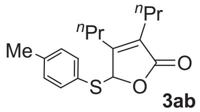
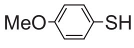
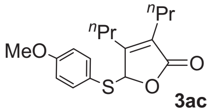
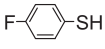
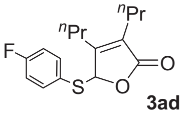
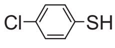
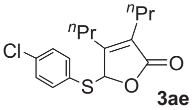
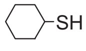
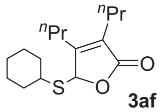
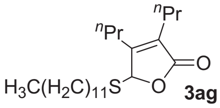
[a] 4-Octyne (3 mmol), PhSH (1 mmol).
[b] Determined by ^{1}H NMR (isolated).
[c] In the absence of DPPE.

Use of 10 mL of acetonitrile improved the yield of **3aa** (48%) (Entry 2). Changing the pressure of CO (1–4 MPa) indicated that 3–4 MPa of CO provided better yields of **3aa** (Entries 4–6). In the absence of DPPE, the yield of **3aa** increased, although the product selectivity of **3aa** versus **4aa** was somewhat lower (Entries 7 and 8).

Table 2 presents the representative results of the thiolative double carbonylation of internal alkynes under the reaction conditions indicated in Entry 8 in Table 1.

Table 2
Double carbonylation with several thiols[a]



Entry	Thiol	Product	Yield (%)[b]
1	PhSH **2a**	 **3aa**	70 (73)
2	 **2b**	 **3ab**	54
3	 **2c**	 **3ac**	59
4	 **2d**	 **3ad**	61
5	 **2e**	 **3ae**	60 (55)
6	 **2f**	 **3af**	49
7	$CH_3(CH_2)_{11}SH$ **2g**	 **3ag**	35

[a] 4-Octyne (3 mmol), RSH (1 mmol), CO (4 MPa), CH_3CN (10 mL), $Co_2(CO)_8$ (9 mol %), 140 °C, 17 h.
[b] Determined by ^{1}H NMR (isolated).

Similar to the case of benzenethiol, aromatic thiols having electron-withdrawing group or electron-donating group could be used for targeted thiolative double carbonylation to give the corresponding α,β-unsaturated γ-arylthio-γ-lactone (**3**) in moderate yields (Entries 2–5). Furthermore, similar conditions could be employed with aliphatic thiols (Entries 6 and 7).

Next, we examined the scope and limitations of this cobalt-catalyzed double carbonylation by using several internal alkynes (Table 3). When 6-dodecyne was used in this double carbonylation, the desired reaction proceeded to give corresponding double carbonylative product in 70% yield (Entry 2). In the cases of unsymmetrical internal alkynes, such as 2-octyne, 6-methyl-2-heptyne, 6-phenyl-2-hexyne, 10-chloro-3-decyne, thiolative