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Rhodium-Catalyzed [2+2+1+1] Cyclocarbonylative Coupling of Alkynes with Carbon Monoxide Affording Tetrasubstituted *p*-Benzoquinones

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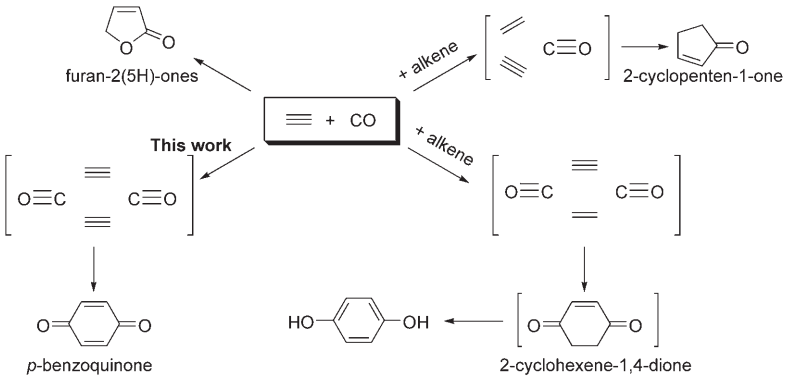
Abstract: In this strategy, the tetrasubstituted benzoquinones have been prepared directly by a [2+2+1+1] cyclocarbonylative coupling reaction of internal alkynes with CO in the presence of $[RhCl(CO)_2]_2$. The low concentration of CO in the reaction is the crucial point for the chemoselective formation of tetrasubstituted benzoquinones in good to high yields. Functional groups such as chloro, methoxy, cyano, vinyl, fluoro, and carboxylate are tolerated under the reaction conditions.

Keywords: alkynes · benzoquinone · carbonylation · cycloaddition · rhodium

Introduction

Transition-metal-catalyzed carbonylation is one of the most important and useful reactions for the synthesis of carbonyl compounds in organic synthesis.[1] The intermolecular cyclocarbonylation from an alkyne, alkene, and CO as well as intramolecular cyclocarbonylation from an enyne or diyne and CO have been proven to be extremely valuable protocols for the synthesis of the unsaturated cyclic ketones, which are widely applied as intermediates for organic synthesis, fine chemicals, and pharmaceutical synthesis. There has been extraordinary progress in these atom-economical cyclization reactions during the last two decades, and it has been disclosed that various structures of unsaturated cyclic ketones can be selectively obtained depending on the use of different substrates, catalysts, and reaction conditions. For example, as shown in Scheme 1, furan-2(5*H*)ones could be selectively formed from the reductive cyclocarbonylation of alkynes in the presence of water catalyzed by a variety of catalyst systems,[2] 2-cyclopenten-1-ones could be obtained by the [2+2+1] cyclocarbonylative coupling of an alkyne, alkene, and CO (Pauson–Khand-type reaction),[3] and 2-cyclohexene-1,4-diones formed through the [2+2+1+1] cyclocarbonylative coupling of an alkyne, alkene, and two molecules of CO; these compounds are intermediates for the synthesis of functionalized hydroquinones.[4]



Scheme 1.

Moreover, the synthesis of bicyclopentenones[3] and the formation of bicyclopentadienones[5] were reported by the direct intramolecular cyclocarbonylation of an enyne or diyne with CO (Scheme 2).

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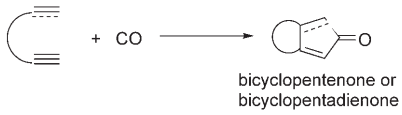
Supporting information for this article is available on the WWW under http://www.chemeurj.org/ or from the author: A general experimental procedure, characterization data, and copies of ^1H, ^{13}C NMR spectra for all products.



Scheme 2.

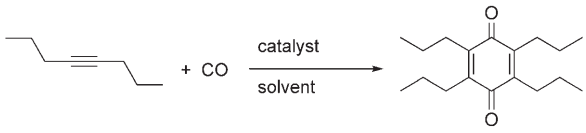
Development of synthetic methods for substituted *p*-benzoquinones is an important research work in organic synthesis,[6] as such types of compounds are not only widely applied as versatile intermediates in diverse organic synthesis, but also widely exist in nature and exhibit various important biological activities.[7] The traditional synthesis of *p*-benzoquinones by oxidizing the substituted phenols has inevitable drawbacks such as: 1) the use of stoichiometric amounts of oxidants which are either expensive or waste-forming processes and 2) the limited availability of substituted phenols. On the basis of retrosynthetic analysis, *p*-benzoquinones can be obtained by the [2+2+1+1] chemoselective cyclocarbonylative coupling of two molecules of an alkyne and two molecules of CO. Therefore, it is an interesting and challenging research work to develop the catalytic system for such cycloaddition reactions.[8,9]

Recently, we have been interested in the development of the transition-metal-catalyzed carbonylation of alkynes. We have developed the $[Ru_3(CO)_{12}]$-catalyzed reductive cyclocarbonylation of internal alkynes in the presence of water to afford 3,4-disubstituted furan-2(5*H*)ones[10] and the rhodium-catalyzed double hydroaminocarbonylation of terminal alkynes with CO and amines to afford 1,4-diamides.[11] As an extension of our efforts in this field, in this paper, we wish to report a [2+2+1+1] cyclocarbonylative coupling strategy of internal alkynes with CO to efficiently synthesize *p*-benzoquinone derivatives in the presence of $[RhCl(CO)_2]_2$.

Results and Discussion

The reaction of 4-octyne (**1a**) with CO under different conditions was examined to screen the optimal reaction conditions for the chemoselective formation of 2,3,5,6-tetrapropyl benzoquinone (**2a**) as summarized in Table 1. We consider that in order to realize the "double" cyclocarbonylation of **1a**, a high CO pressure might be favorable for **2a** formation.

Table 1. Catalytic cyclocarbonylation of 4-octyne with carbon monoxide.[a]



1a **2a**

Entry	Catalyst [mol%]	Solvent	Other conditions[b]	Yield of **2a** [%][c]
1	$[RhCl(CO)_2]_2$ (2.5)	toluene	CO (5.0 MPa), 130 °C for 24 h	<5
2	$[RhCl(CO)_2]_2$ (2.5)	toluene	CO (1.0 MPa), 130 °C for 24 h	20
3	$[RhCl(CO)_2]_2$ (2)	$CHCl_2CHCl_2$	CO (1.0 MPa), 120 °C for 24 h	10
4	$[RhCl(CO)_2]_2$ (2)	toluene	CO atmosphere, 120 °C for 24 h	18
5	$[RhCl(CO)_2]_2$ (2)	$CHCl_2CHCl_2$	CO atmosphere, 120 °C for 24 h	27
6	$[RhCl(CO)_2]_2$ (2.5)	$CHCl_2CHCl_2$	CO bubbling, 120 °C for 24 h	33
7	$[RhCl(CO)_2]_2$ (2.5)	BuOBu	CO bubbling, 120 °C for 24 h	13
8	$[RhCl(CO)_2]_2$ (2.5)	DMSO	CO bubbling, 120 °C for 24 h	<5
9	$[RhCl(CO)_2]_2$ (2.5)	$CHCl_2CHCl_2$	Ph_3P (10 mol%), CO bubbling, 120 °C for 24 h	0
10	$[RhCl(CO)_2]_2$ (2.5)	$CHCl_2CHCl_2$	Bu_3N (10 mol%), CO bubbling, 120 °C for 24 h	0
11	$[RhCl(CO)_2]_2$ (2.5)	$CHCl_2CHCl_2$	CO bubbling, 140 °C for 24 h	72
12	$[RhCl(CO)_2]_2$ (2.5)	$CHCl_2CHCl_2$	CO/N_2 (ca. 1:1) bubbling, 140 °C for 15 h	71
13	$[RhCl(CO)_2]_2$ (2.5)	$CHCl_2CHCl_2$	CO/N_2 (ca. 1:1) bubbling, 140 °C for 24 h	94 (90)
14	$RhCl_3 \cdot 3H_2O$ (5)	$CHCl_2CHCl_2$	CO/N_2 (ca. 1:1) bubbling, 140 °C for 15 h	22

[a] Reactions were carried out by using 1.0 mmol of **1a** in 1.0 mL of solvent. [b] Bubbling rate: ≈1.5–2.0 mL min^{-1}. [c] GC yield (isolated yield) based on the amount of **1a** used.

formed and that without the formation of any other carbonylated products, **1a** was recovered (entry 1). However, unexpectedly, when the same reaction was repeated under a mild initial CO pressure (1.0 MPa) in toluene at 130 °C and in 1,1,2,2-tetrachloroethane (TCE) at 120 °C for 24 h, **2a** was obtained in 20 and 10% GC yields, respectively (entries 2 and 3). These results encouraged us to examine the same experiment with a lower CO pressure.

As shown Table 1, under a CO atmosphere, the yield of **2a** could be substantially increased (entries 4 and 5). Thus we can ascertain that the low concentration of CO in the reaction system favors the formation of **2a**. As a matter of fact, when bubbling CO gas (1.5–2.0 mL min^{-1}) through the reaction solution a higher yield of **2a** resulted (33% GC yield, entry 6). In order to further enhance the formation of **2a**, the effects of solvents and additives were also briefly examined. It was found that the use of the coordinated solvents (for example, BuOBu and DMSO), and ligands (for example, PPh_3 and Et_3N) led to the decrease or complete loss of the catalytic activity of $[RhCl(CO)_2]_2$ for the formation of **2a** (entries 7–10).

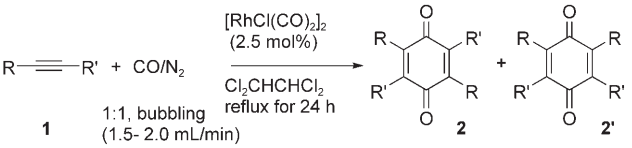
The catalytic activity of $[RhCl(CO)_2]_2$ in TCE could be greatly improved by increasing the reaction temperature. An increase of the reaction temperature up to 140 °C resulted in the formation of **2a** in 72% GC yield (entry 11) after 24 h. Surprisingly, an identical result was obtained by bubbling CO/N_2 (CO/N_2 = ca. 1:1, ≈1.5–2.0 mL min^{-1}) at this

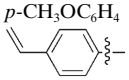
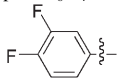
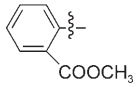
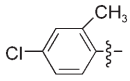
temperature in a shorter time (15 h, entry 12). Therefore, a prolonged reaction time up to 24 h led to a satisfactory yield of **2a** (94% GC), which was isolated in 90% yield (entry 13). Furthermore, under similar conditions, $RhCl_3 \cdot 3H_2O$ also showed catalytic activity to give **2a** in 22% GC yield (entry 14).

A number of tetrasubstituted *p*-benzoquinones could be synthesized by the present catalytic procedure by the cyclocarbonylative coupling of a variety of internal alkynes with CO under the reaction conditions as indicated in entry 13 of Table 1. As summarized in Table 2, the yields of *p*-benzoquinones are sensitive to the nature of alkyne substitution. The reactions of 3-hexyne (**1b**) and 5-decyne (**1c**) with carbon monoxide gave the cycloadducts **2b** and **2c** in 87 and 96% isolated yields, respectively (Table 2, entries 1 and 2). The yields are similar to that obtained from **1a**. However, when 2-octyne (**1d**), 1-phenyl-2-octyne (**1e**), and 1-(4-ClC_6H_4)-2-octyne (**1f**) were employed, the two regioisomers of *p*-benzoquinones were isolated in relatively low total yields (Table 2, entries 3–5).

Aryl and alkyl-substituted asymmetrical internal alkynes also reacted efficiently to produce the corresponding *p*-benzoquinones of two regioisomers, and the electronic effect of the substituent on the aromatic ring is very significant. The monophenyl (**1g–j**), monoelectron-rich aryl-substituted (**1k–n**) internal alkynes seem to be good substrates for the cyclocarbonylative coupling reaction to afford the corresponding *p*-benzoquinones in good to high yields (Table 2, entries 6–14). The cyclocarbonylative coupling reaction of electron-deficient monoaryl-substituted internal alkynes (**1p–s**) with carbon monoxide also occurred, but afforded relatively low yields of the desirable products (Table 2, entries 15–18). As evident from Table 2, this catalytic system can tolerate various functional groups, such as methoxy, cyano, vinyl, chloro, fluoro, and ester.

Table 2. Cyclic carbonylation of internal alkyne.[a]



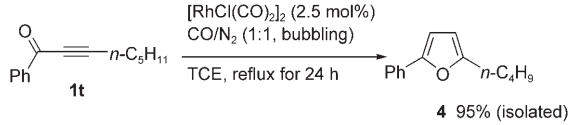
Entry	Starting material	R	R′	Product	Yield [%][b] (2+2′)	2/2′
1	**1b**	C_2H_5	C_2H_5	**2b**	87	
2	**1c**	n-C_4H_9	n-C_4H_9	**2c**	96	
3	**1d**	n-C_5H_{11}	CH_3	**2d**	28	48:52[c]
4	**1e**	$PhCH_2$	n-C_5H_{11}	**2e**	35	53:47[c]
5	**1f**	p-$ClC_6H_4CH_2$	n-C_5H_{11}	**2f**	40	51:49[d]
6	**1g**	Ph	CH_3	**2g**	89	80:20[d]
7	**1h**	Ph	C_2H_5	**2h**	85	84:16[d]
8	**1i**	Ph	n-C_4H_9	**2i**	65 (33+32)	
9	**1j**	Ph	n-C_5H_{11}	**2j**	59 (27+32)	
10	**1k**	p-$CH_3C_6H_4$	n-C_5H_{11}	**2k**	87 (45+42)	
11	**1l**	p-$CH_3OC_6H_4$	n-C_6H_{13}	**2l**	80 (40+40)	
12	**1m**	p-$CH_3OC_6H_4$	n-C_5H_{11}	**2m**	86 (40+46)	
13	**1n**	p-$CH_3OC_6H_4$	$NC(CH_2)_3$	**2n**	53	49:51[d]
14	**1o**		n-C_5H_{11}	**2o**	50 (26+24)	
15	**1p**	p-ClC_6H_4	n-C_5H_{11}	**2p**	40	59:41[c]
16	**1q**		n-C_5H_{11}	**2q**	45	59:41[c]
17	**1r**		n-C_5H_{11}	**2r**	31	75:25[d]
18	**1s**		n-C_5H_{11}	**2s**	26	61:39[c]

[a] Reactions were carried out by using 1.0 mmol of **1** in 1.0 mL of solvent under reflux for 24 h. [b] Isolated yield. [c] Isomer ratio was determined by GC analysis. [d] Isomer ratio was determined by ^1H NMR spectroscopy.

In the present [2+2+1+1] cyclocarbonylative coupling reaction, when an unsymmetrical internal alkyne was employed, the formation of two possible regioisomers was observed as expected. The ratio of two regioisomers could be determined by either ^1H NMR spectroscopy (Table 2, entries 5–7, 13, and 17) or GC analysis (Table 2, entries 3–4, 15–16, and 18). In the cases of **1i–m** and **1o** used, two regioisomers could be separated by preparative TLC isolation.[13]

Interestingly, when 1-benzoyl-1-heptyne (**1t**) was subjected to the same reaction conditions, the corresponding *p*-benzoquinone derivative was not formed at all. Instead, 2-*n*-butyl-5-phenylfuran (**4**) was isolated in 95% yield (Scheme 3).[14]

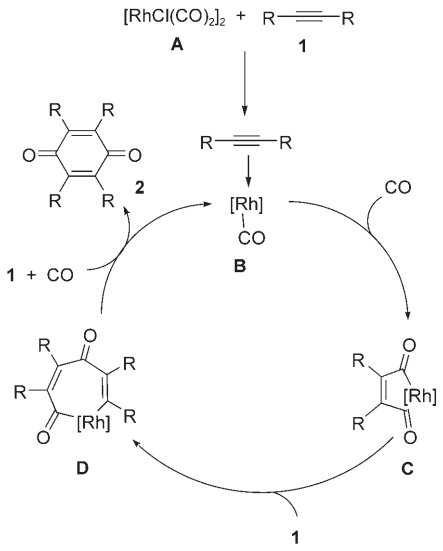
As described above, monoaryl-substituted internal alkynes undergo the [2+2+1+1] cyclocarbonylative coupling reaction to afford the corresponding *p*-benzoquinones. Unfortunately, the coupling reaction of alkynes possessing two bulky groups, such as 1,2-diarylated alkynes, could not take place under the same reaction conditions. The formation of other carbonylated products was not observed either and diarylacetylene was recovered completely.



Scheme 3.

Moreover, the present Rh(I)-catalyzed cyclocarbonylative addition conditions are not effective for both terminal alkynes and propiolate derivatives. In the case of terminal alkynes employed, the reaction gave a mixture of (cyclo)trimers. The reaction of propiolate derivatives resulted in the formation of the cyclotrimer of alkynes as the major product, accompanied with the formation of dimers confirmed by GCMS analysis.

On the basis of the previous reports on the formation of maleoylmetal complexes from alkynes and two molecules of CO,[15] and *p*-benzoquinones from the reaction of maleoylmetal complexes with alkynes,[8] a proposed mechanism involving the formation of rhodacycle intermediates is depicted in Scheme 4. At first, the reaction of rhodium(I) dimer **A**



Scheme 4. Proposed mechanism for [2+2+1+1] cyclocarbonylative coupling of an internal alkyne and carbon monoxide.

with an alkyne gives the alkyne-coordinating intermediate **B**. The oxidative coupling of the coordinated alkyne and CO to the rhodium generates a five-membered rhodacycle **C**, followed by insertion of the alkyne into the rhodium–carbon bond to form a seven-membered rhodacycle **D**. The carbon–carbon bond formation by the reductive elimination furnishes benzoquinone **2** and regenerates intermediate **B**.

From our present investigation, it is apparent that the catalytic formation of *p*-benzoquinones is sensitive to the concentration of CO in the reaction, and the most important factor for high chemoselective formation of *p*-benzoquinones is to perform the cyclocarbonylation reaction under a low concentration of CO. It is likely that over a certain value of CO concentration, CO competes with the alkyne for coordination to the rhodium center to restrain the formation of intermediates **B** and/or **D**.

Conclusion

We have developed an efficient catalyst system to realize the straightforward synthesis of tetrasubstituted benzoquinones in modest to high yields by [2+2+1+1] cyclocarbonylative coupling of internal alkynes with CO in the presence of $[RhCl(CO)_2]_2$. The present research work has extended the utility of the cyclocarbonylative coupling reaction of alkynes with CO to provide a facile and atom-economic method for synthesizing various tetrasubstituted *p*-benzoquinones, some of which are not easily prepared by the traditional synthetic method.

Experimental Section

A representative procedure for the [2+2+1+1] cyclocarbonylative coupling of 4-octyne (1a) with CO

Formation of 2,3,5,6-tetra-n-*propyl-1,4-benzoquinone (**2a**)*: A mixture of 4-octyne (110.0 mg, 1.0 mmol) and $[RhCl(CO)_2]_2$ (9.8 mg, 0.025 mmol) in 1,1,2,2-tetrachloroethane (1.0 mL) was bubbled with carbon monoxide and nitrogen (CO/N_2 = ca. 1:1, ≈1.5–2.0 mL min^{-1}) with stirring at room temperature for 5 min. The resulting yellow solution was then refluxed with continued bubbling of the gas mixture (oil bath temperature was 140 °C) for 20 h. After GC and GCMS analyses of the reaction mixture, volatiles were removed under a reduced pressure and the residue was subjected to silica-gel column chromatography (eluting with cyclohexane and then with a diethyl ether/hexane mixture (3≈5:100)) to afford **2a** (124.1 mg, 90 %) as a yellow viscous oil. GC analyses of the reaction mixture disclosed the formation of **2a** in 94 % yield.

Acknowledgements

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[12] Other rhodium complexes such as $[RhCl(PPh_3)_3]$, [RhCl(CO)(dppb)] (dppb = 1,4-bis(diphenylphosphino)butane), and $[RhCl(cod)(PPhMe_2)]$ (cod = 1,5-cyclooctadiene) did not give **2a** at all.

[13] The structures of two regioisomers could be confirmed clearly by ^{1}H and ^{13}C NMR spectroscopy, see the Supporting Information.

[14] CuI catalysis of the same transformation was reported see: A. V. Kel′in, V. Gevorgyan, *J. Org. Chem.* **2002**, *67*, 95–98.

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