# Rhodium-Catalyzed Intramolecular Pauson-Khand Reaction

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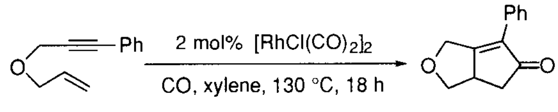
A rhodium dinuclear carbonyl complex, $[RhCl(CO)_2]_2$, serves as a catalyst of the intramolecular Pauson-Khand reaction. 1,6-Enynes are converted to cyclopentenone derivatives in high yield by heating in the presence of the catalyst under an atmospheric pressure of CO.

The Pauson-Khand reaction has been an attractive method for the preparation of cyclopentenone derivatives from three components, that is, alkynes, alkenes, and CO.[1] Nonetheless, in the classical Pauson-Khand reaction, a stoichiometric quantity of $Co_2(CO)_8$ was needed. Since 1990, some reports dealing with the catalytic Pauson-Khand reaction have appeared in which cobalt, titanium, and ruthenium complexes serve as catalysts.[2-5] Most of these reactions were, however, conducted under a medium or high pressure of CO. Only $Co_2(CO)_8$ with high-intensity visible light system and the titanocene complexes could serve as catalysts under an atmospheric pressure of CO.[2e,3] Thus, development of more practically useful catalyst has been desirable for the Pauson-Khand reaction.

We thought that rhodium complexes would have an ability to promote the Pauson-Khand reaction, because rhodium belongs to the same group with cobalt. When a xylene solution of an allyl propargyl ether **1a** and 2 mol% of $[RhCl(CO)_2]_2$, a commercially available rhodium dinuclear carbonyl complex, was heated at 130 °C under an atmospheric pressure of CO, a cyclocarbonylated product **2a** was obtained in 88% yield without the recovery of the starting material (eq 1). Thus, the reaction is the first example of the rhodium-catalyzed intramolecular Pauson-Khand reaction. This rhodium-catalyzed method can be carried out with a simple equipment; with the use of a balloon filled with CO, without the use of an autoclave.

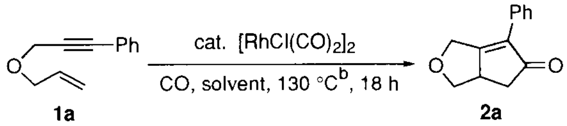


(1)

**1a** **2a** 88%

Then, we examined the solvent effect and the results are summarized in Table 1. While *N*,*N*-dimethylacetamide and chlorobenzene were not suitable for this reaction, the reaction in dibutyl ether or in xylene at 130 °C permitted an efficient conversion of the enyne **1a** to the cyclopentenone **2a** as a sole isolated product. The reaction could be conducted by employing only 0.5 mol% of the rhodium complex without a significant loss of yield.

**Table 1.** Solvent effect on the rhodium-catalyzed intramolecular Pauson-Khand reaction of **1a**[a]

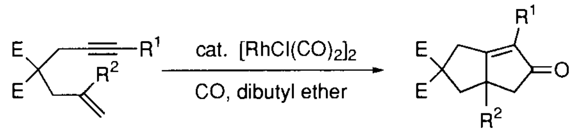


**1a** **2a**

| $[RhCl(CO)_2]_2$ mol% | Solvent | Yield of **2a** % |
|---|---|---|
| 2 | *N*,*N*-dimethylacetamide | 14[c] |
| 2 | chlorobenzene | 63 |
| 2 | *p*-xylene | 88 |
| 2 | dibutyl ether | 89 |
| 1 | dibutyl ether | 82 |
| 0.5 | dibutyl ether | 83[d] |

[a] Reactions were carried out according to the procedure described in the text. [b] The oil bath temperature. [c] **1a** was recovered (50%). [d] 20.5 h.

**Table 2.** Cyclopentenones **2** from 1,6-enynes **1**[a]



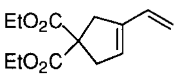
**1** E = $CO_2Et$ **2**

| $R^1$ | $R^2$ | | $[RhCl(CO)_2]_2$ | Temp.[b] | Time | Yield of **2** | |
|---|---|---|---|---|---|---|---|
| | | | mol% | °C | h | | % |
| Ph | H | (**1b**) | 5 | 90 | 9 | (**2b**) | 97[c] |
| Ph | H | (**1b**) | 1 | 130 | 16 | (**2b**) | 94 |
| Et | H | (**1c**) | 1 | 130 | 18 | (**2c**) | 91 |
| H | H | (**1d**) | 1 | 150 | 12 | (**2d**) | 41 |
| TMS | H | (**1e**) | 5 | 150 | 18 | (**2d**) | 41 |
| | | | | | | (**2e**) | 35 |
| Ph | Me | (**1f**) | 5 | 160 | 15 | (**2f**) | 71 |

[a] Reactions were carried out according to the procedure described in the text. [b] The oil bath temperature. [c] THF was used as a solvent.

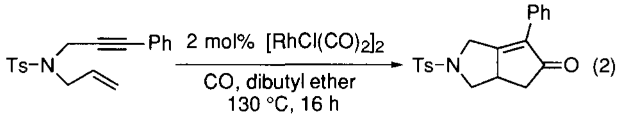
Various 1,6-enynes which has *gem*-disubstituted groups were converted to cyclopentenones by using the rhodium complex and the results are summarized in Table 2. Phenyl- and alkyl-substituted acetylenes **1b**,**c** reacted to afford the corresponding cyclocarbonylated products **2b**,**c** in high yield, respectively. Especially the enyne **1b** reacted even in refluxing THF (the oil bath temperature 90 °C), however, it was difficult to obtain reproducible results. An enyne **1d** having a terminal acetylene moiety was converted to a cyclopentenone derivative **2d** in 41% yield by heating at 150 °C with the complete consumption of **1d**. Murai et al. have already reported that the enyne **1d** cycloisomerizes to form diethyl 3-ethenyl-3-cyclopentene-1,1-dicarboxylate (**3**) by the catalytic use of $[RhCl(CO)_2]_2$,[6] while under our reaction conditions **3** was formed only in 9% yield. A trimethylsilyl-substituted acetylene

**1e** gave the corresponding cyclopentenone **2e** and the desilylated product **2d** in 76% total yield. An enyne **1f** possessing a methyl group at the internal olefinic carbon gave the desired cyclocarbonylated product **2f** in 71% yield by heating at 160 °C along with cycloisomerized products **4** and **5**.[7]



**3**

As shown in eq 2, an *N*,*N*-allyl propargyl sulfonamide **1g** also gave the corresponding cyclopentenone derivative **2g** in high yield.



**1g** Ts = $SO_2$-*p*-Tol **2g** 92%

The representative experimental procedure is as follows: To a dibutyl ether (4 ml) solution of $[RhCl(CO)_2]_2$ (3.9 mg, 0.01 mmol) was added a dibutyl ether (6 ml) solution of diethyl 8-nonen-3-yne-6,6-dicarboxylate (**1c**, 266.7 mg, 1.00 mmol) under an atmospheric pressure of CO, and the mixture was heated at 130 °C (the oil bath temperature) for 18 h. After evaporation of the solvent, the crude products were purified by thin-layer chromatography (silica gel, hexane : ethyl acetate = 4 : 1, three times) to afford diethyl 8-ethyl-7-oxobicyclo[3.3.0]oct-8(1)-ene-3,3-dicarboxylate (**2c**, 268.7 mg, 91% yield).

In conclusion, the commercially available rhodium dinuclear carbonyl complex, $[RhCl(CO)_2]_2$, catalyzes the intramolecular Pauson-Khand reaction under an atmospheric pressure of CO.

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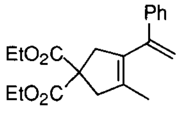
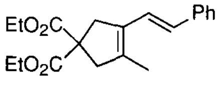
7 The structures and yields of cycloisomerized products **4** and **5**[6] were as follows.



**4** 15%



**5** trace