

Rhodium-Catalyzed Intramolecular Pauson-Khand Reaction

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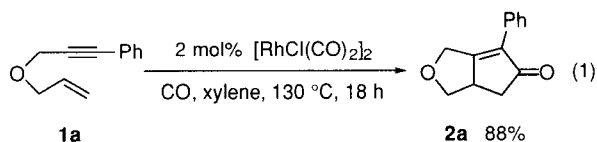
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A rhodium dinuclear carbonyl complex, $[\text{RhCl}(\text{CO})_2]_2$, serves as a catalyst of the intramolecular Pauson-Khand reaction. 1,6-Enynes are converted to cyclopentenone derivatives in high yield by heating in the presence of the catalyst 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 $\text{Co}_2(\text{CO})_8$ 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 $\text{Co}_2(\text{CO})_8$ 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 $[\text{RhCl}(\text{CO})_2]_2$, 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.



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.

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

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

$[\text{RhCl}(\text{CO})_2]_2$ mol%	Solvent	Yield of 2a %
2	<i>N,N</i> -dimethylacetamide	14 ^c
2	chlorobenzene	63
2	<i>p</i> -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.

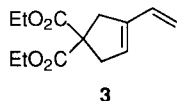
Table 2. Cyclopentenones **2** from 1,6-enynes **1**^a

R ¹	R ²	$[\text{RhCl}(\text{CO})_2]_2$ mol%	Temp. ^b °C	Time h	Yield of 2 %
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

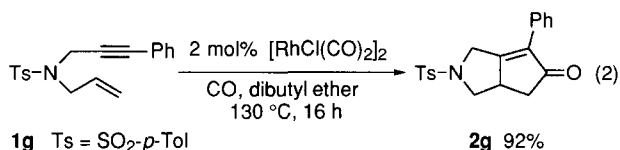
^a Reactions were carried out according to the procedure described in the text. ^b The oil bath temperature. ^c THF was used as a solvent.

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 $[\text{RhCl}(\text{CO})_2]_2$,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



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



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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