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New protocol for the catalytic Pauson–Khand reaction induced by molecular sieves

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Abstract—The catalytic Pauson–Khand reaction is favoured in the presence of molecular sieves. This easy protocol probably involves the adsorption of carbon monoxide by the zeolites, making it possible to effect the reaction in the absence of CO atmosphere. © 2002 Elsevier Science Ltd. All rights reserved.

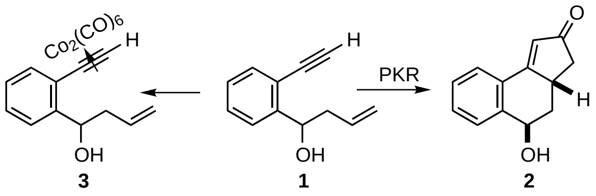
There has been a considerable effort in recent years to achieve protocols for a catalytic version of the Pauson–Khand reaction.[1] Some of the reports dealing with this process use severe reaction conditions,[2] non-commercial metal complexes[3] or other chemical additives.[4] Recently, Livinghouse[5] and Krafft[6] have introduced new methods that reach good results using 1 atmosphere of carbon monoxide at 65°C. Still, these methods are used only with a few substrates appropriately *gem*-disubstituted or bearing heteroatoms that act as soft ligands. Also, chemical additives such as cyclohexylamine or amine *N*-oxydes are often necessary.

The scope of the stoichiometric version of the Pauson–Khand reaction has increased in past years as new promoters have been found.[7] In particular we have recently introduced zeolites as new efficient promoters for Pauson–Khand reactions.[8] Herein we report a new protocol for a catalytic version of the Pauson–Khand reaction showing the important role of the molecular sieves in the process. It is well known that zeolites are able to adsorb small molecules such as CO and this may help in the recovery of the cobalt catalyst and thus in improving the catalytic cycle.

Aromatic enynes like **1** have been introduced by us as new substrates for the intramolecular Pauson–Khand reaction (Scheme 1).[9] This substrate reacts in a totally diastereoselective manner in the stoichiometric Pauson–Khand reaction.[10] In order to achieve a catalytic version of this process, compound **1** was submitted to the set of reaction conditions summarised in Table 1. Considering the above mentioned studies,[5,6] we fixed the reaction temperature at 65°C for all reactions, and the CO pressure at 1 atm. Cobalt octacarbonyl was used as supplied, without purification.

As shown in Table 1, there are no significant differences between toluene and DME as solvents; so we chose toluene for the following reactions. At the beginning we found some erratic behaviour with the results. Thus there was an increase in yield when raising the amount of cobalt to 10%, that seemed excessive. We realised we had opened a new bottle of cobalt carbonyl. When repeating the reactions with 5% of the new cobalt, yields increased (Table 1, entries 1, 2, 5, 6). The use of preformed cobalt–hexacarbonyl complex **3** also gives good results but does not improve the use of commercial cobalt–octacarbonyl. The conclusion is that molecular sieves always increase significantly the conversion and yield of the reaction.

Molecular sieves have been used in several catalytic organic transformations[11] such as epoxidation of allylic alcohols (Sharpless epoxidation),[12] or Diels–Alder reac-



Scheme 1.

Keywords: Pauson–Khand reaction; zeolites; catalytic.

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Table 1. Reaction conditions for the PKR of compound **1**

No	Solvent[a]	Catalyst	Mol. sieves[b]	Yield (%)[c]	
				2	**1**
1	Toluene	5% $Co_2(CO)_8$	–	20/35[d]	45/25[d]
2	Toluene	5% $Co_2(CO)_8$	Yes	40/60[d]	40/25[d]
3	Toluene	10% $Co_2(CO)_8$	–	40	30
4	Toluene	10% $Co_2(CO)_8$	Yes	70	10
5	DME	5% $Co_2(CO)_8$	–	15/20[d]	55/50[d]
6	DME	5% $Co_2(CO)_8$	Yes	40/55[d]	30/20[d]
7	DME	10% $Co_2(CO)_8$	–	45	30
8	DME	10% $Co_2(CO)_8$	Yes	70	10
9	Toluene	5% **3**	–	40	45
10	Toluene	5% **3**	Yes	50	50
11	Toluene	10% **3**	–	50	35
12	Toluene	10% **3**	Yes	70	0

[a] THF was also tested observing decomposition of starting material.

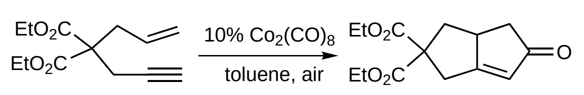
[b] Powdered molecular sieves preheated in oven at 125°C for 4 h and cooled under argon. Two times the mass of the starting material.

[c] Of pure material with correct spectroscopic data (^1H, ^{13}C NMR, IR).

[d] Results with 'old'/'new' (recently opened) cobalt hexacarbonyl.

tions.[13] In the Pauson–Khand process, molecular sieves may act by interacting with the enyne and stabilising a pretransition state or they may protect the catalyst. Nevertheless, we believe that adsorption of CO by the sieves may be responsible for this favourable effect. To support this, we submitted compound **4** to three reactions in air atmosphere with 10% cobalt octacarbonyl: blank reaction, addition of molecular sieves, and addition of molecular sieves heated to 200°C and cooled under carbon monoxide (Scheme 2).

The results show an important increase in conversion with sieves, reaching 65% with the pre-treated zeolite. The latter conditions may be considered as the first efficient catalytic conditions of the Pauson–Khand reaction without any CO atmosphere.[14] Thus we heated a batch of molecular sieves at 200°C (3 h) and cooled them under a CO atmosphere, and used them in PKR of several substrates depicted in Table 2. The reactions were carried out in toluene and in an air atmosphere with 10% cobalt octacarbonyl (conditions A). The results were compared with the best reaction conditions of Table 1 (entry 4) which correspond to 10% cobalt carbonyl in toluene with molecular sieves (conditions B), and a blank essay without sieves and under 1 atm of CO in toluene (conditions C).[15] The results show that yields improve remarkably when using molecular sieves, and that conditions A also are an interesting alternative to traditional reactions under a CO atmosphere, although they do not reach the results of conditions B under CO.



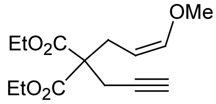
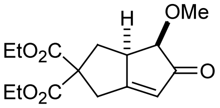
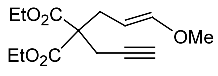
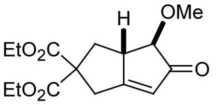
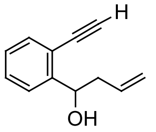
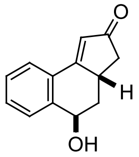
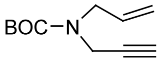
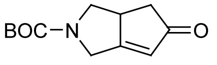
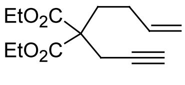
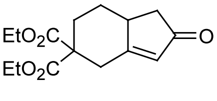
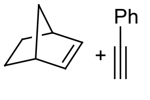
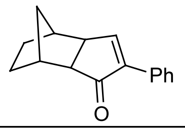
4 **5**

Without M.S.: 15%
With M.S.: 30%
With M.S. pretreated with CO: 65%

Scheme 2.

In conclusion, molecular sieves improve the conversion of the catalytic Pauson–Khand reaction, probably due to their ability to adsorb and keep carbon monoxide which makes it possible to effect the reaction in the absence of a CO atmosphere. We will further report the complete study on the role of the zeolites in this reaction.

Table 2. Compared catalytic PKR of different substrates

No.	Starting Material	Product	Yield (%)		
			A	B	C
1[a]			80	90	50
2[a]			73	88	59
2			58	70	40
3			50	70	40
4			70	85	50
5			60	70	41

[a] The reaction product showed the relative stereochemistry indicated. No other isomers were detected in the crude mixture. The configuration was assigned by n.O.e experiments.

Acknowledgements

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15. Experimental procedure: Conditions A (Table 2): A flask containing powdered 4 Å molecular sieves was heated (200°C, 3 h) and cooled under CO atmosphere. These molecular sieves (twice the mass of the enyne) are added to a flask containing a solution of 1.00 mmol of the enyne **1** in toluene (10 mL) at room temperature. To this solution, 0.10 mmol of $Co_2(CO)_8$ was added and the resulting mixture was stirred for 18 h at 65°C. After filtration through celite, the solvent was evaporated under vacuum and the crude product purified by flash chromatography (hexane/EtOAc mixtures). Conditions B: Same as conditions A but using non pre-treated molecular sieves and with the stirring in a CO atmosphere (balloon). Conditions C: Same as conditions B without molecular sieves.