



## Amine Induced Pauson-Khand Reaction

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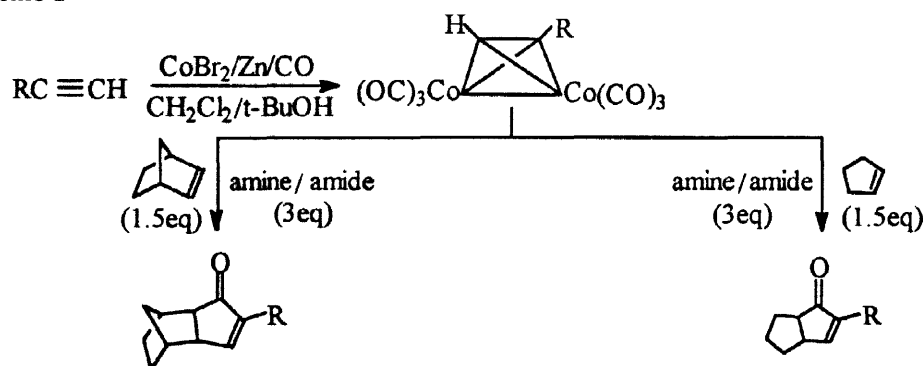
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**Abstract:** The Pauson-Khand reaction of alkyne-dicobalt hexacarbonyl complexes, prepared *in situ* in dichloromethane / *t*-BuOH using cobalt(II) bromide / Zn / CO(1atm) / alkyne, takes place readily at 25°C in the presence of certain amines. © 1997 Elsevier Science Ltd. All rights reserved.

The cobalt mediated cyclisation of alkyne, alkene, and CO has emerged as an elegant way for the synthesis of cyclopentenones.<sup>1</sup> Recently, we have developed a method for *in situ* generation of  $(RC\equiv CH)Co_2(CO)_6$  complex in THF and reported its applications.<sup>2,3</sup> Since THF promotes the disproportionation of  $Co_2(CO)_8$ <sup>4</sup> we have been looking for an alternate solvent system. It has been reported that the reduction of  $CoI_2$  in *t*-BuOH/toluene mixture by Zn metal in presence of CO at atmospheric pressure gives  $Co_2(CO)_8$  in 38% yield after 24h.<sup>5</sup> We have observed that the  $(RC\equiv CH)Co_2(CO)_6$  complex, prepared *in situ* using  $CoBr_2$  and Zn in  $CH_2Cl_2/t$ -BuOH at atmospheric pressure and room temperature by bubbling CO, gives the corresponding cyclopentenones on heating with norbornene (1.5 eq) in reasonable yields (R=C<sub>5</sub>H<sub>11</sub>, 80%, R=Ph, 78%).

We have also observed that tetramethylethylenediamine (TMEDA),  $\alpha$ -methylbenzylamine and dimethylformamide (DMF) promote the Pauson-Khand reaction of the alkyne-cobalt complexes prepared *in situ* in this way (Scheme 1).

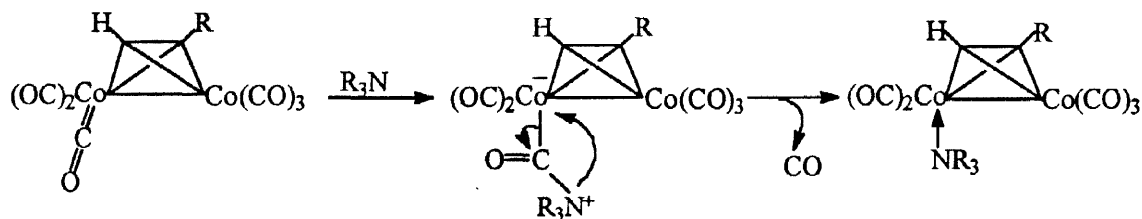
Scheme 1



amine/amide	R	Yield	amine/amide	R	Yield
TMEDA	C <sub>5</sub> H <sub>11</sub>	53%	TMEDA	C <sub>5</sub> H <sub>11</sub>	30%
C <sub>6</sub> H <sub>5</sub> CH(CH <sub>3</sub> )NH <sub>2</sub>	Ph	55%	C <sub>6</sub> H <sub>5</sub> CH(CH <sub>3</sub> )NH <sub>2</sub>	Ph	32%
DMF	C <sub>8</sub> H <sub>17</sub>	52%	DMF	C <sub>8</sub> H <sub>17</sub>	32%

The cyclopentenones were obtained in lower yields than that obtained under refluxing conditions. Also, the yields are somewhat low compared to that realised in the reactions with other known promoters such as amine oxides, DMSO etc. at 25°C.<sup>6</sup> However, the simplified one-pot Pauson-Khand reaction procedure under ambient conditions using amines should be synthetically useful. The following is the general procedure: A mixture of CoBr<sub>2</sub> (4.4g, 20 mmol), Zn (1.35g, 20 mmol) and RC≡CH (10 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (50 mL)/t-BuOH (1.5 mL) was stirred while bubbling CO at 25°C for 8h. The CO atmosphere was replaced by dry static nitrogen. Olefin (15 mmol), amine or amide (30 mmol) were added and the contents were stirred for 3h at 25°C. The mixture was washed successively with dilute HCl, water and brine solution. The organic extract was dried over anhydrous MgSO<sub>4</sub>. It was concentrated and the products were separated by silica gel (100-200 mesh) chromatography using hexane/ethyl acetate as eluent. In all reactions, varying amounts of unidentified cobalt carbonyl complexes and small amounts of unidentified organic products were also formed.

Presumably, the amine may form a weak complex which could facilitate the Pauson-Khand reaction.<sup>7</sup> However, use of chiral α-methylbenzylamine in the transformations reported here did not result in asymmetric induction.



We have found that the Pauson-Khand reaction can be also carried out without using t-BuOH, by preparing the complex in the presence of amine (1.5 mL) in CH<sub>2</sub>Cl<sub>2</sub> (50 mL) and following the procedure described as above (cyclopentenone yields: norbornene/TMEDA, R= C<sub>5</sub>H<sub>11</sub>, 50%, norbornene/α-methylbenzylamine, R= C<sub>8</sub>H<sub>17</sub>, 52%, cyclopentene/α-methylbenzylamine, R = Ph, 32%).

In conclusion, the simple, convenient procedure for preparation of alkyne-Co<sub>2</sub>(CO)<sub>6</sub> complexes from readily accessible bench-top chemicals and the amine induced Pauson-Khand reaction under ambient conditions should make the methods described here attractive for synthetic applications.

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