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A Sub-Stoichiometric Version of the Pauson-Khand Reaction

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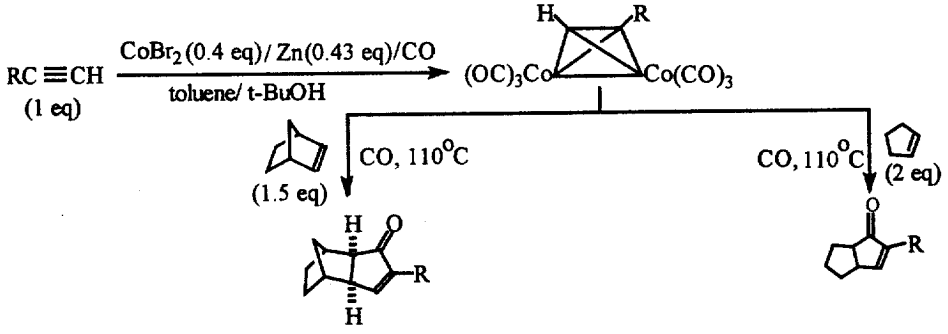
Abstract: A new protocol for the Pauson-Khand reaction using alkyne-$Co_2(CO)_6$ complexes prepared from sub-stoichiometric amounts of $CoBr_2$ and Zn at atmospheric pressure of carbon monoxide is described.

Keywords: Pauson-Khand reaction; Cyclopentenones; Cobalt Carbonyl.

The Pauson-Khand reaction of an alkyne, alkene and carbon monoxide, mediated by cobalt carbonyl to yield cyclopentenones, has become a widely used transformation in synthetic organic chemistry.[1] Several advances of this reaction have been reported in recent years.[2] We have developed methods for *in situ* generation of alkyne-$Co_2(CO)_6$ complexes in different solvents[3] and reported their synthetic applications.[4] In recent years, there have been several reports describing the use of cobalt, titanium and rhodium complexes in catalytic amounts, along with CO, in Pauson-Khand cyclopentenone synthesis.[5,6] These reactions are, however, generally carried out under medium or high pressure of CO. We wish to report here that the Pauson-Khand reaction can be readily carried out with an alkyne-$Co_2(CO)_6$ complex, generated *in situ* using sub-stoichiometric amounts of $CoBr_2$ and Zn, in toluene/t-BuOH at atmospheric pressure of CO. The results are summarised in Scheme 1.

Scheme 1



R	time	Yield
Ph	24h	83%
Ph	12h	67%
n-C_5H_{11}	24h	88%
n-C_8H_{17}	24h	85%

R	time	Yield
Ph	24h	32%
n-C_6H_{13}	24h	30%
n-C_8H_{17}	24h	35%

As expected, the yields are moderate to good in the reactions with norbornene but poor with the less reactive cyclopentene. In all reactions, some amounts of unidentified carbonyl compounds were also

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obtained. In reactions carried out using phenyl acetylene, the corresponding trimerised product was also obtained in 5-10% yield. Also, use of 0.2 equivalents each of $CoBr_2$ and Zn with PhC≡CH (1 eq) and norbornene (1.5 eq) resulted in lower yield (40%) of the corresponding cyclopentenone.

The following is the general procedure: A mixture of $CoBr_2$ (0.88g, 4 mmol), Zn (0.28g, 4.3 mmol) and RC≡CH (2 mmol) in toluene (50 mL)/t-BuOH (1.5 mL) was stirred while bubbling CO at 25°C for 5h. Alkyne (8 mmol) and olefin (15-20 mmol) were added and the contents were stirred for 24h at 110°C while bubbling CO at atmospheric pressure. Water (20 mL) was added and the organic layer was separated. The aqueous layer was extracted with ether (50 mL). The combined organic extract was washed with water (20 mL), brine solution (20 mL) and dried over anhydrous $MgSO_4$. It was concentrated and the products were separated by silica gel (100-200 mesh) chromatography using hexane/ethyl acetate as eluent. The yields of products are based on the amount of alkyne used.

We have carried out a reaction using TMEDA in the place of t-BuOH with PhC≡CH and norbornene. The yield of the cyclopentenone (67%) obtained is somewhat lower under these conditions. We have also carried out the reaction in CH_2Cl_2/t-BuOH solvent system at 45°C under atmospheric pressure of CO for 24h. Again, the corresponding cyclopentenone was obtained only in lower yield (48%) compared to that obtained at 110°C in toluene. In conclusion, the simple method described here for the Pauson-Khand reaction using sub-stoichiometric amounts of $CoBr_2$ at atmospheric pressure of CO should be attractive for synthetic applications.

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