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MOLYBDENIUM MEDIATED PREPARATION OF CYCLOPENTENONES

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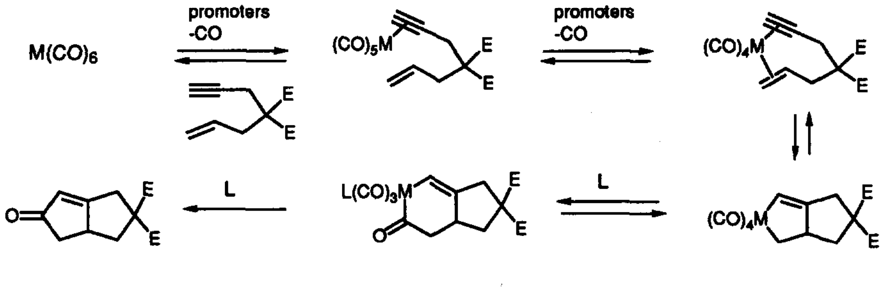
SUMMARY; *Cocyclization of alkynes, alkenes and carbon monoxide was achieved in the presence of a stoichiometric amount of molybdenium hexacarbonyl and excess of dimethylsulfoxide. This process will constitute another version of Pauson-Khand reaction.*

Cocyclization of alkynes with alkenes and carbon monoxide by transition metals has become one of the most popular reactions for the preparation of cyclopentenones. Since the first success of the synthesis of cyclopentenones from alkynes and alkenes in either intramolecular[1] or intermolecular manner[2] employing dicobalt octacarbonyl (known as Pauson-Khand reaction), a number of variation with different metals, including zirconium,[2] titanium,[4] nickel[5] (in this reaction isonitriles were used instead of carbon monoxide), iron[6a] and tungsten[6b] have appeared in the literature. Each variation has its own advantages and/or disadvantages in terms of the scope of substrate compatibility, yield and practicality. Among them, Pauson-Khand reaction has played a key role in this class of reactions because of its operational simplicity and broad range of functional group compatibility. The synthetic significance of this reaction has been greatly enhanced by the finding of promoters, such as N-methylmorpholine-N-oxide,[7] trymethylamine-N-oxide[8] and DMSO.[9]

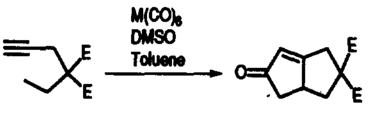
Meantime, we envisioned that promoters mentioned above would facilitate the formation of vacancy on group VI metal carbonyl also for incoming ligands, such as alkynes and/or alkenes, either oxidatively or nonoxidatively. A possible mechanism operating for this goal is given in Scheme 1. Based on the proposed mechanism, we also envisaged that this reaction could be catalytic in the presence of external carbon monoxide, which has been well conceived conceptually but rarelly reallized.[10]



Scheme1

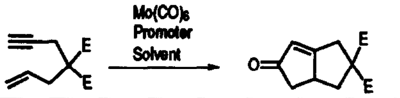
First we have examined that following metals, such as chromium, molybdenium and tungsten carbonyls, for the cyclization with enyne substrate (**1**) in toluene. As we anticipated, the reaction did not proceed at all or produced a multitude of compounds with the most starting matreials remained in the absence of promoters regardless what metals were employed. With DMSO each metal carbonyl behaves differently. Chromium carbonyl was still totally reluctant to work for this purpose, and tungsten carbonyl, from which removal of carbon monoxide has been difficult, provided a cyclopentenone (**2**) in poor yield (12%), But it is fortunate enough to find that molybdenium carbonyl provided a clean reaction to yield a cyclopentenone (**2**) in 76% yield. The reaction by heating a mixture of enyne (**1**) and molybdenium carbonyl (1.2eq) together with DMSO (5-10eq) in toluene at 100°C produced a cyclopentenone (**2**) with the deposition of dark blue metal clusters.[11] (Table1)

Table I: Examination of Metal Carbonyls for the Preparation of Cyclopentenones



Metals	eq. of DMSO	Reaction Time	Temperature	Results
$Cr(CO)_6$	10	24 hr	100°C	No Reaction
$Mo(CO)_6$	10	8 hr	100°C	76%
$W(CO)_6$	10	24 hr	100°C	12%

Table II: Examination of Promoters for the Cycloadditions



Promoters	Solvents	Reaction Time	Temperature	Results
N-methylmorpholine N-oxide	toluene		rt	no reaction
			100 °C	a complex mixture
DMSO(10eq)	toluene	8 hr	100 °C	76%
Dithiane(10eq)	toluene	10 hr	100 °C	36% no s.m. left
CH_3CN(10 eq)	toluene	10 hr	100 °C	a mixture of tarry products
CH_3CN	CH_3CN	10 hr	100 °C	a mixture of tarry products

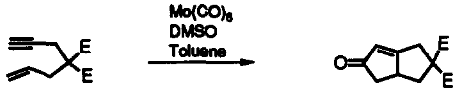
Next, we tried to sort out the best promoters. Tertiaryamine N-oxide, which is known to release CO_2 by oxidation of CO, failed to promote the reaction at ambient temparature but gave a complex mixture of products at elevated temparature (100°C). The reaction in acetonitrile or in toluene with 10eq of acetonitrile yielded a tarry product. Dithiane worked for the reaction for the consumption of all the starting matrials but the cyclization yield is too low (36% yield) to be accepted. Thus, we have set the standard reaction condition with 5-10 eq of DMSO at 100°C in toluene (Table 2).

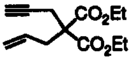
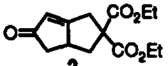
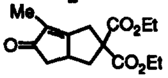
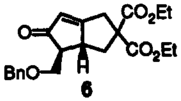
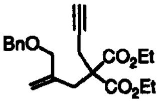
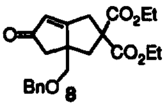
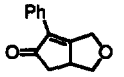
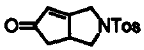
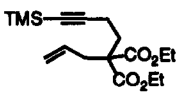
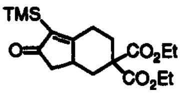
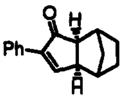
A representative experimental procedure is given as follow; A mixture of enyne (**1**) (1.12g, 5.0mmol), molybdenium carbonyl (1.58g, 6.0mmol), which is sparingly soluble at ambient temparature, and DMSO (1.8mL, 25mmol, 5eq) in toluene was heated at 100°C. Heating was continued untill all the starting matrial disappeared (8-12h), at which time usually dark blue precipitate had been deposited. The mixture was passed through a small plug of silica gel and the filtrate was concentrated *in vacuo* and purified by silica gel chromatography, if necessary, to give the product (**2**) (960mg, 3.8mmol) in 76%yield.

As one might notice from the experimental procedure, operation of this reaction is much simpler than and the efficiency is as good as any previous one. The reaction proceeded smoothly in the intramolecular manner with monosubstituted olefines regardless of the substitution pattern of alkynes (entry 1 and 2). The 1,2-disubstituted alkenes are also good substrates in this reaction together with various alkynes (entry 3). But 1,1-disubstituted alkenes were inert under this condition over prolonged period (36hr) (entry 4). Heteroatom bridged enynes produced oxobicyclic compound (**10**)[12] and azabicyclic compound (**12**)[13] from the corresponding substrates (**9**) and (**11**) respectively in evenly good yield (65 and 69%). However, preparation of [5.6] bicyclic system was another unsuccessful case (entry 7, starting material was unchanged).

Intermolecular reaction between acetylenes and olefines is a pleasant bonus. Actually, these results are far beyond our expectation because we predicted that the competition favored to acetylene over olefines for the second ligation would cause complications. In a reaction of 1 to 1 ratio of phenylacetylene and norbonene, a mixture of 1,3,5-triphenylbenzene (18)[14] in 45% yield together with uncharacterized side products as a major portion and the cyclopentenone (17) in 18% yield. Encouraged by this result, a reaction in a ratio of 1 to 10 of an acetylene (15) and an olefine (16) was carried out and cyclopentenone (17) was obtained in 50% yield based on the acetylene and (18) in 10% yield along with an inseparable mixture of side products.

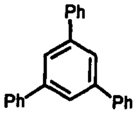
Table III; Examples of the Molybdenium Mediated Cyclopentenone Formation



Entry	Enynes	Products	Temp	Reaction Time	Yield
1	 1	 2	100°C	12h	76%
2	 3	 4	100°C	12h	80%
3	 5	 6	100°C	12h	62%
4	 7	 8	100°C	30h	0%
5	 9	 10	100°C	12h	65%
6	 11	 12	100°C	12h	69%
7	 13	 14	100°C	24h	0%
8	 15  16 1 : 1	 17	100°C	12h	18%
9	1 : 10		100°C	12h	50%

Although the resulting metal obtained after a cycle for the cyclopentenones can be converted to carbonylated species under the CO pressure, preliminary examination revealed that the catalytic turnover under either 1atm. or 30 atm. of CO is disappointment. Further trials for the catalytic process are underway. At the moment the mechanistic aspects look unclear. In a reaction with (1) in the presence of a sulfoxide (19) (5eq) as a promoter, we observed the recovery of the sulfide (20) was nearly quantitative along with a cyclopentenone (2) in 18% yield. Thus, we presumed the removal of carbon monoxide from the metal happened by oxidative way.[9]

In conclusion, we, herein, present a new version of *Pauson-Khand like process* leading to cyclopentenones employing molybdenium carbonyl together with DMSO in toluene for the first time. This process is quiet efficient and far superior to others in terms of practicality.



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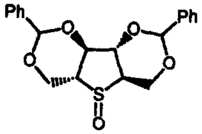

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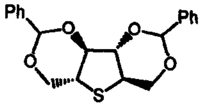

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14. The regiochemistry of this compound was assigned unambiguously by comparison of ^{1}H NMR, ^{13}C NMR and mass spectral data to those in the literature.

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