Tetrahedron Letters, Vol.30, No.5, pp 595-596, 1989 0040-4039/89 $3.00 + .00
Printed in Great Britain Pergamon Press plc

A Simple Convenient Synthesis of Alkyne-$Co_2(CO)_6$ Complexes and their utilization in the Pauson-Khand Cyclopentenone Synthesis

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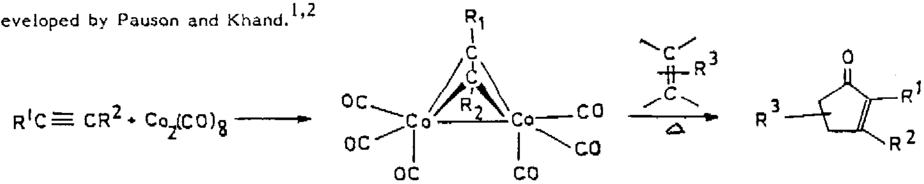
Abstract: Reduction of anhydrous $CoBr_2$ in THF with zinc under carbon monoxide atmosphere at room temperature followed by treatment with alkynes gives the corresponding alkyne-cobalt carbonyl complexes, which on reaction with olefins give the corresponding cyclopentenone in moderate to good yields.

The formation of cyclopentenones in a single step from an alkene, alkyne and carbon monoxide moieties has been discovered and developed by Pauson and Khand.[1,2]



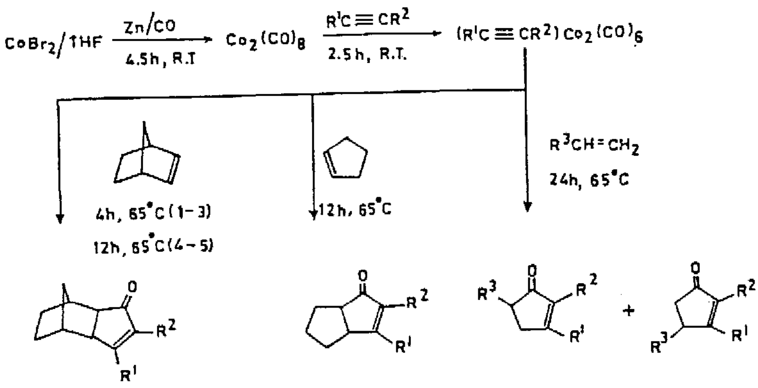
The Pauson-Khand cyclopentenone synthesis has been utilized in crucial steps in the total synthesis[3-5] of several cyclopentanoid natural products. We wish to report here a simple in situ synthesis of alkyne-cobalt carbonyl complexes using simple bench top chemicals and utilization of such complexes in the Pauson-Khand cyclopentenone synthesis.

We have recently reported that the addition of $NaBH_4$ into anhydrous $CoCl_2$ in THF while bubbling carbon monoxide at atmospheric pressure gives cobalt carbonyl species which on treatment with aqueous NaOH yields the $^-Co(CO)_4$ reagent.[6] The $^-Co(CO)_4$ reagent generated in this way has been utilized in the carbonylation of benzylhalides.[6] It was of interest to us to examine whether dicobaltoctacarbonyl reagent can be generated following such simple reductions in the presence of carbon monoxide at atmospheric pressure. We have observed that the species produced by the $NaBH_4$ reduction is not the $Co_2(CO)_8$ species since it failed to give the Pauson-Khand cyclization with phenyl acetylene and norbornene.[7]

It has been reported that the reduction of CoI_2 in t-butanol/toluene mixture by zinc metal in the presence of carbon monoxide at atmospheric pressure gives $Co_2(CO)_8$ after 24h.[8] We have observed that the anhydrous $CoBr_2$ did not undergo reduction under these conditions. However, when the reduction of anhydrous $CoBr_2$ by zinc dust was carried out in anhydrous THF, the dicobaltoctacarbonyl was formed quantitatively as indicated by the isolation of its diphenylacetylene complex, $(PhC\equiv CPh)Co_2(CO)_6$ in 85% yield. (mp 105°C, Lit.[9] mp 109°C). We have observed[10] that the representative alkyne complexes prepared in situ in this way undergo the Pauson-Khand cyclization with representative alkenes to give cyclopentenone derivatives in yields as good as those realised following Pauson-Khand original procedure[1,2] (Chart I). The following is the general procedure. A mixture of anhydrous $CoBr_2$ (10 mmol) and zinc dust (11 mmol) in THF (125 ml) was stirred while bubbling carbon monoxide (generated by dropwise addition of formic acid to conc. H_2SO_4 at 90°C) for 4.5h. The carbon monoxide atmosphere was replaced by dry static nitrogen and 4-octyne (5 mmol) was added and stirred for 2.5h at room temperature. Norbornene (7.5 mmol) was added under nitrogen and the contents were refluxed for 12h. The reaction mixture was added to 20 ml of H_2O and extracted with ether. The organic extract was dried over $MgSO_4$ and concentrated. The residue was chromatographed on a silica gel column and the ketone was isolated in 78% yield.

In the runs with the less reactive alkenes (i.e. cyclopentene, 1-decene and 1-octene) the alkynes also undergo trimerization[11] to give the 1,2,4 and 1,3-5 aryl or alkyl benzenes to the extent of 25-45%. These hydrocarbon products were readily separated from the desired Pauson-Khand cyclopentenones by chromatography on a silica gel column using hexane as eluent.

Chart I



Yield

(1) $R^1=H$, $R2=Ph$ 80%
(2) $R^1=H$, $R^2=C_8H_{17}$ 92%
(3) $R^1=H$, $R^2=C_6H_{13}$ 88%
(4) $R^1=Ph$, $R^2=Ph$ 38%
(5) $R^1=C_3H_7$, $R^2=C_3H_7$ 78%

Yield

(6) $R^1=H$, $R^2=C_8H_{17}$ 58%
(7) $R^1=H$, $R^2=Ph$ 47%

Yield

(8) $R^1=H$, $R^2=Ph$, $R^3=C_8H_{17}$ (Mixture) 26%
(9) $R^1=H$, $R^2=C_5H_{11}$, $R^3=C_6H_{13}$ (Mixture) 30%

In addition to the utilization in Pauson-Khand reaction, the $Co_2(CO)_8$ is useful as a protecting and stabilizing group for alkyne moieties[12] and it also serves as the starting material in the synthesis of several useful cobaltcarbonyl derivatives.[13] Accordingly, it is anticipated that the present in situ synthesis of the metal carbonyl using bench-top chemicals under atmospheric pressure of carbon monoxide would make the synthetic methods utilizing such metal carbonyl derivatives more attractive since in addition to making the metal carbonyl readily accessible for synthetic applications, it also alleviates the problems involved in the storing and handling of metal carbonyl derivatives.

Acknowledgement: We thank the CSIR, New Delhi for financial support of this research work. We also thank the UGC for Special Assistance Programme and COSIST support.

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(Received in UK 14 November 1988)