Abstract

This thesis deals with the results of the investigations carried out on the “Development of Organic Synthetic Methods Using Cobalt Carbonyl Reagents.” It comprises of three chapters. Each chapter is subdivided into three parts. “Introduction,” “Results and Discussion” and “Experimental section” along with references. The work described in this thesis is exploratory in nature and the chapters are arranged in the order the investigations were executed.

Chapter 1 describes the preparation of alkylne-Co$_2$(CO)$_6$ complexes via reduction of CoBr$_2$ with Zn in the presence of CO in CH$_2$Cl$_2$/t-BuOH or toluene/t-BuOH for applications in Pauson-Khand cyclopentenone synthesis (Scheme 1). Recent developments in the Pauson-Khand reaction are briefly reviewed in the Introductory section. To facilitate the discussion, methods of preparation of (alkynel)Co$_2$(CO)$_6$ complexes are also briefly reviewed.

Scheme 1

It has been observed that the amines/amides promote the Pauson-Khand reaction (alkynel)Co$_2$(CO)$_6$ complexes prepared in this way in CH$_2$Cl$_2$/t-BuOH solvent
system at 25 °C (Scheme 2). Whereas the use of norbornylene gave the corresponding cyclopentenones in 52-58% yields, cyclopentene afforded the products in 30-32% yields.

Scheme 2

![Scheme 2](image)

The Pauson-Khand reactions were also carried out in CH$_2$Cl$_2$ in the presence of amines such as TMEDA, α-methylbenzylamine. The yields of cyclopentenones obtained were similar to the reactions that were carried out using CH$_2$Cl$_2$ and t-BuOH.

The Pauson-Khand reactions carried out using sub-stoichiometric amounts of CoBr$_2$ and Zn (Scheme 3) are also described in chapter 1. The cyclopentenones were obtained in good yields when norbornylene was used as olefin. In the case of cyclopentene, the products were obtained in 30-35% yields.

Scheme 3

![Scheme 3](image)
In chapter 2, results of the Investigations carried out on the reactions of \((\text{alkyne})\text{Co}_2(\text{CO})_6\) complexes without using an externally added olefin are described. The reactions of such complexes are briefly reviewed. The \((\text{alkyne})\text{Co}_2(\text{CO})_6\) complexes prepared \textit{in situ} in toulene/t-BuOH solvent system by the reduction of \(\text{CoBr}_2\) with Zn in the presence of CO and alkynes give cyclopentenones in 10-50\% yields on heating at \(110^\circ\text{C}\) (Scheme 4).

Scheme 4

![Scheme 4](image)

Interestingly, the reaction of \((\text{RC}=\text{CSiMe}_3)\text{Co}_2(\text{CO})_6\) complexes in \textit{toluene/t-BuOH} gave the corresponding \textit{silyl} substituted cyclopentadienones in 30-40\% yields (Scheme 5). In all cases, symmetrically substituted cyclopentadienones were obtained except in phenyl substituted alkynyl silane, in which both symmetrically and \textit{unsymmetrically} substituted cyclopentadienones were obtained.

Scheme 5

![Scheme 5](image)

Interestingly, the reaction of \((\text{alkyne})\text{Co}_2(\text{CO})_6\) complexes with promoters such as \textit{DMSO, TMEDA} in \textit{CH}_2\text{Cl}_2/t-\text{BuOH} solvent system gave the corresponding
dicyclopentadienones in 15-20% yields at 25 °C (Scheme 6). Possible mechanistic pathways and intermediates involved in these transformations are described.

Scheme 6

In chapter 3, the hydroformylation reactions of olefins using CoBr₂/Zn/CO in toluene/t-BuOH solvent system are described. A brief account on the hydroformylation reaction using cobalt carbonyl reagents is presented in the introductory section.

We have observed that the hydroformylation of alkenes can be carried out with the cobalt carbonyl reagent prepared using CoBr₂, Zn and CO in toluene/t-BuOH solvent mixture. Acyclic terminal olefins give both normal and branched isomers of aldehydes in 1:1 ratio in moderate yields under these conditions (Scheme 7). In these reactions, alkanes (25-30%) were also isolated. Results of efforts to optimize the reaction conditions are also described.

Scheme 7

The intermediacy of species such as HCo(CO)₄ is indicated in the hydroformylation reaction (Scheme 7). Accordingly, the use of such reagent system for other synthetic applications of the cobalt carbonyl species prepared in this way was
also examined. It was observed that certain allylalcohols undergo isomerization reaction to form ketones in 78-85% yields (Scheme 8).

Scheme 8

The results are discussed in comparison with that reported in the literature.