

The Carbonylations of Cyclohexene with Carbon Dioxide

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Abstract : It is introduced that the carbonylations of cyclohexene with CO₂ can take place under ambient conditions by catalysis of Co(acac)₂ in the presence of ultraviolet irradiation .

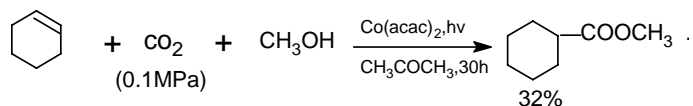
Keywords: Carbon dioxide, carbonylation, photocatalysis .

Carbon dioxide, a natural and inexpensive source of functional carbon units, shows potential abilities for the functionalization of organic substrate. The high stability of CO₂, however, and the lack of reliable methods of activation, considerably restrict its applications¹. In recent years transition metal catalyzed reactions of carbon dioxide aimed at the utilization of CO₂ as building block in organic synthesis have attracted considerable attentions, because carbon dioxide is the biggest carbon source on earth and the basis of all biochemical organic synthesis processes. Carbon dioxide is nowadays obtained as a by-product in technical processes. Chemistry for catalytic activation of CO₂ is still underdeveloped². Yet a lot of progresses have been made with the process of research work. For instance, the telomerization of butadiene with carbon dioxide yielding lactones, acids and esters has been the subjects of several investigation. The reactions of CO₂ with olefins, however, are now mainly limited to those reactions in which expensive metal catalysts (Ru, Pd) and higher temperatures (90~165 °C)³ are necessary.

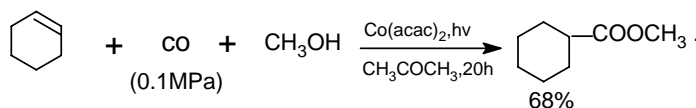
Recently photocatalyzed carbonylations have made great advance, which would make some reactions take place under ambient conditions that should have been completed in higher temperatures and pressures, and catalyzed by expensive metal catalysts in general situations^{4,5}. However, our experiments have established that the reactions of CO₂ with olefins can surprisingly give some results similar to CO in the presence of ultraviolet under ambient conditions by using inexpensive metal Co(acac)₂ as catalysts⁶.

A quartz photo-reactors containing cyclohexene (*ca.*0.1M) and 10 % (mol) of bis(pentane-2,5-dionato)cobalt(II), [Co(acac)₂], in CH₃OH-CH₃COCH₃ (3:1, V/V, 400ml). The solution was irradiated by a 400W high pressure mercury lamp (GGY-400, Philips & Yaming Corp.) under 0.1MPa CO₂ at room temperature, and by ultraviolet irradiation 30 hours. The isolated major product exhibits pertinent I.R. absorptions at 1750cm⁻¹. GC of

the major product give exactly the same retention time as authentic sample by co-injection , and the M.S. spectra of the major product show the expected molecular ions and fragmentation patterns. The reaction is as following :



The preliminary experiments showed that acetone acts as sensitizer and the reaction can not proceed in absence of it. It can be seen that esters can be produced by reaction of CO₂ and olefins under ambient conditions without using expensive metal catalysts, which could make it applicable. Compared to the carbonylations of CO with olefins carried out in our laboratory , the yields and selectivities of the reactions of CO₂ are lower .



In order to get higher yields and selectivities , the selection of sensitizer and the effects of acid and base on the reaction , and the mechanism of the reactions are under investigation.

It is expected that the carbonylations of CO₂ provide a new way to utilize CO₂ and be promising through extensive experiment research and mechanism studies .

Acknowledgment

We are indebted to the Natural Science & Technology Foundation Council of Liaoning Province , and Open Laboratory of Carbon Resource Utilization of Dalian University of Technology , for the generous financial support .

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Received 28 July 1998

Revised 24 May 1999