Copper(I) Cyanoacetate as a Carrier of Activated Carbon Dioxide

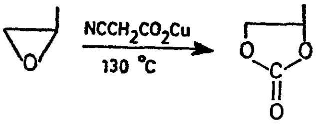
By Tetsuo Tsuda, Yoshiki Chujo, and Takeo Saegusa*
(*Department of Synthetic Chemistry, Faculty of Engineering, Kyoto University, Kyoto, Japan*)

Summary Copper(I) cyanoacetate acts as a carrier of activated CO_2, transferring its CO_2 unit to propylene oxide to produce propylene carbonate quantitatively.

Recently, the interest in organic reactions of CO_2 also involving transition-metal complexes has increased, and the use of a transition-metal complex acting as a CO_2 carrier is relevant to biological biotin-dependent carboxylations where the carboxy-biotinyl-enzyme is known to function as a carrier of activated CO_2.[1] Several isolable transition-metal complexes which fix CO_2 reversibly under mild conditions have been reported,[2] but there is no report of effecting an organic reaction of CO_2 fixed in this type of transition-metal complex. We have already reported the quantitative decarboxylation of copper(I) cyanoacetate producing an isolable cyanomethylcopper(I):[3] $NCCH_2CO_2Cu \rightarrow NCCH_2Cu + CO_2$, and we now report quantitative transcarboxylation from copper(I) cyanoacetate to propylene oxide to produce propylene carbonate.

A mixture of $NCCH_2CO_2Cu$ (0·91 mmol) and propylene oxide (18·2 mmol) was heated at 130 °C for 10 h under nitrogen in a sealed tube. Propylene carbonate was produced in 83% yield based on $NCCH_2CO_2Cu$. The reaction could also be carried out in $HCONMe_2$ [$NCCH_2CO_2Cu$ (1·18 mmol) and propylene oxide (5·90 mmol) in dimethylformamide (1 ml) at 130 °C for 10 h gave a 94% yield], but reaction in benzene gave a lower yield. A relatively high temperature is needed and the reaction at 120 °C is slow.

These results indicate that $NCCH_2CO_2Cu$ acts as a carrier of activated CO_2. Transcarboxylation to active methylene compounds by magnesium methyl carbonate is well known and is characterized by the formation of a magnesium enolate stabilized by chelation with an adjacent carboxylate anion.[4] The present study is characterized by its reaction path in that the decarboxylated species effects the reaction between the liberated CO_2 and the substrate, providing another new type of transcarboxylation by means of a CO_2 carrier. For comparison, the reaction of magnesium methyl carbonate (0·73 mmol) with propylene oxide (3·65 mmol) at 130 °C for 8 h gave propylene carbonate in only 7·2% yield.



The easy decarboxylation of $NCCH_2CO_2Cu$ owing to the presence of an electron-withdrawing cyano-group suggests that $NCCH_2Cu$ plays an important role in the formation of propylene carbonate, and in fact it was found to catalyse the production of propylene carbonate from CO_2 and propylene oxide. $NCCH_2Cu$ (0·73 mmol) and propylene oxide (21·9 mmol) were heated at 130 °C for 8·5 h under CO_2 (*ca.* 2·5 mmol CO_2) to give propylene carbonate in 247% yield based on $NCCH_2Cu$. The reaction of $NCCH_2CO_2Cu$ and propylene oxide under CO_2 also proceeded catalytically. The reaction of propylene oxide with no copper complex in acetonitrile under CO_2 at 130 °C did not form propylene carbonate.

The exact mechanism for the formation of propylene carbonate cannot yet be elucidated, partly because $NCCH_2Cu$ is unstable under the conditions used. However, it is interesting that the nature of the ligand on copper is important for the reaction, $NCCH_2Cu$ being the most effective complex; CuCN, CuCl, CuOAc, $CuSBu^n$, $CuOBu^t$, and metallic copper were ineffective. $CuC{\equiv}CPh$ gave propylene carbonate only in 2·1% yield.

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