

## Letter

---

### Carbonylation of Benzyl Chloride to Phenylacetic Acid and its Ester using Water-soluble Ru(III)-EDTA Complex Catalyst

M. M. TAQUI KHAN\*, S. B. HALLIGUDI and S. H. R. ABDI

*Discipline of Coordination Chemistry and Homogeneous Catalysis, Central Salt and Marine Chemicals Research Institute, Bhavnagar 364 002 (India)*

(Received June 1, 1987; accepted September 24, 1987)

#### *Introduction*

The technology of homogeneous transition metal-catalyzed carbonylation reactions is being currently used for large volume chemicals [1]. The carbonylation of benzyl chloride to give phenylacetic acid finds many applications in organic synthesis [2], and the product is used as a perfume in waxes and honey. Carbonylation of aryl halides with CO under ambient conditions has been studied using  $\text{Ni}(\text{CO})_4$ ,  $\text{NaCo}(\text{CO})_4$  or nickel(II)-thiourea complex as catalyst in combination with a base [3 - 10]. However, the yields of the carbonylation products were very poor. The carbonylation of benzyl halides in the presence of a base using Pd(II) and Pd(0) complexes [11] gave a better yield of the carbonylated products. Recently, the carbonylation of benzyl chloride with a Pd(II) catalyst had been reported [12] to give an overall conversion of 65% in 24 h. This corresponds to a low turnover number.

In our study of carbonylation catalysis in aqueous systems we have examined the carbonylation of benzyl chloride in ethanol-water mixed solvent system. The reaction proceeds at 80 °C and 20 atm of CO to yield phenylacetic acid and its ester, with a turnover frequency of 44 mol product per hour.

#### *Experimental*

Ru(III)-EDTA complex was prepared and characterised by known methods [13]. The solvents used were pure A.R. grade and were distilled before use. The CO gas cylinder was obtained from BOC, U.K.

The carbonylation of benzyl chloride was conducted in a 300 ml stainless steel high pressure reactor (Parr Instrument Co.) with provisions for automatic temperature control and an agitator system. The reaction mixture was prepared by adding 10 ml of benzyl chloride (0.869 mol) to an 8:2 mixture of ethanol-water solvent. The catalyst Ru(III)-EDTA (2 mmol) was

---

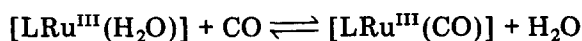
\* Author to whom correspondence should be addressed.

then added to the solution and the volume was made up to 100 ml. The reactor was flushed twice with CO gas. After the desired temperature 80 °C was attained, the pressure of CO gas was adjusted to the required level of 20 atm. Initial and final samples of the reaction mixture were withdrawn, and liquid samples were also withdrawn at different intervals for product analysis. The products were analysed by TLC techniques, and the progress of the reaction was monitored till the benzyl chloride spot on TLC plate disappeared. The products were then separated by column chromatography and were analysed as phenylacetic acid and ethylphenyl acetate. A 100% conversion was achieved in 9 h.

### Results and discussion

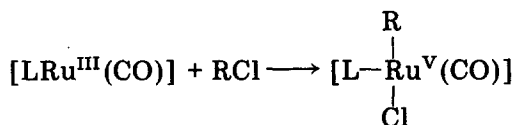
The carbonylation of benzyl chloride catalyzed by Ru(III)-EDTA catalyst system gave 100% conversion to the desired products phenylacetic acid and ethylphenyl acetate in 9 h.

A possible mechanism of the reaction, based on our observations, is given in Scheme 1.

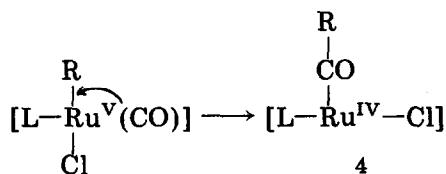


1

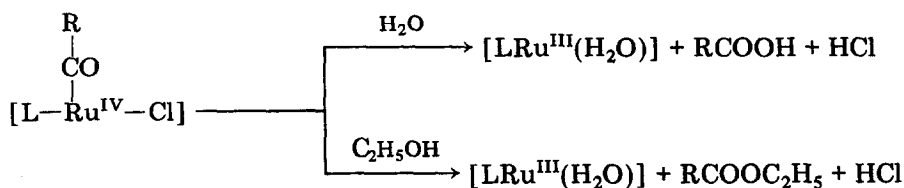
2



3



4



L = H-EDTA (protonated ethylenediaminetetraacetic acid)

R = C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>-

Scheme 1.

In the above mechanism, the first step is the formation of carbonyl complex 2 by the displacement of H<sub>2</sub>O. Complex 2 is a paramagnetic Ru(III) species with  $\mu_{\text{eff}}$  of 1.96 B.M. at 25 °C, corresponding to a  $(t_{2g})^5$  Ru(III) one unpaired spin configuration. The  $\nu(\text{Ru}-\text{CO})$  of the complex is observed at 1960 cm<sup>-1</sup> in the IR spectrum. The carbonyl complex 3 activates RCl to form a mixed ligand benzyl-carbonyl-chloro complex 4. The formation of this complex is envisaged as the rate-determining step, which is similar to that of methanol carbonylation catalyzed by rhodium complex [14]. Insertion of CO in the M-C bond of 4 forms the acyl intermediate 5, the hydrolysis of which results in the formation of phenylacetic acid or its ester. In this reaction the ratio of acid to ester obtained is 2:3, which is lower than the ratio of water:ethanol in the solvent 1:4. This indicates a facile reaction of 5 with water as a nucleophile rather than ethanol.

### References

- 1 G. W. Parshall, *Homogeneous Catalysis*, Wiley, New York, 1980, p. 77.
- 2 P. Karrer, *Organic Chemistry*, 4th edn., Elsevier, Amsterdam, 1950, p. 524.
- 3 E. J. Corey and L. S. Hegedus, *J. Am. Chem. Soc.*, **91** (1969) 1233.
- 4 L. Cassar and M. Foa, *Inorg. Nucl. Chem. Lett.*, **6** (1970) 291.
- 5 M. Nakayama and T. Mizorogi, *Bull. Chem. Soc. Jpn.*, **44** (1971) 508.
- 6 L. Cassar, M. Foa and A. Gardano, *J. Organometall. Chem.*, **121** (1976) 7761.
- 7 R. F. Heck and D. S. Breslow, *J. Am. Chem. Soc.*, **85** (1963) 2779.
- 8 G. P. Chiusoli, M. Dubini, M. Ferraris, F. Guerrieri, S. Merzoni and G. Mondelli, *J. Chem. Soc., C* (1968) 2289.
- 9 A. Schoenberg and R. F. Heck, *J. Am. Chem. Soc.*, **96** (1974) 7761; *idem*, *J. Org. Chem.*, **39** (1974) 3327.
- 10 T. Kobayashi and M. Tanaka, *J. Organometall. Chem.*, **205** (1981) C27.
- 11 M. Hidai, T. Hikita, Y. Wada, Y. Fujikura and Y. Uchida, *Bull. Chem. Soc. Jpn.*, **48** (1975) 2075.
- 12 B. M. Choudhary, N. Prabhakar Reddy and M. Z. Jamil, *Polyhedron*, **5** (1986) 911.
- 13 M. M. Taqui Khan, Arun Kumar and Z. Shirin, *J. Chem. Res. (S)* 1986) 130.
- 14 J. F. Roth, J. H. Craddock, A. Hershman and F. E. Paulik, *Chemtech.*, (1971) 600.