

Letter

# Epoxidation of cyclohexene catalyzed by copper(II) complexes under Mukaiyama's conditions

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In 1990 Mukaiyama and associates [1] described an effective catalytic system able to promote the epoxidation of olefins by dioxygen at ambient conditions (Scheme 1).

The success of this synthesis depends critically on the presence of an aldehyde, which appears to act as a sacrificial oxygen scavenger. The metal species reported to be catalytically active were  $\beta$ -diketonato complexes of  $\text{Ni}^{\text{II}}$ ,  $\text{Co}^{\text{II}}$  and  $\text{Fe}^{\text{III}}$ .

We have recently described the synthesis and homopolymerization of bis-2-acetoacetoxyethylmethacrylate copper(II),  $\text{Cu}(\text{aaema})_2$ , (**1**) [2] which was synthesized within the framework of a project aimed at the preparation of polymer-supported Mukaiyama's catalysts.

We find that **1** is an active and very selective catalyst in the epoxidation of cyclohexene, its catalytic activity and selectivity being comparable with those of its  $\beta$ -diketonate and  $\beta$ -ketoamidate analogs,  $\text{Cu}(\text{acac})_2$  (**2**) (acac = acetylacetonate) and  $\text{Cu}(\text{pcpaa})_2$  (**3**) (pcpaa = *N-p*-chlorophenyl-acetoacetamidate) [3], respectively (Table 1).

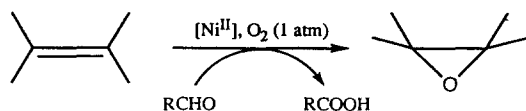


Table 1

Epoxidation of cyclohexene promoted by various copper(II) catalysts in dichloroethane in the presence of isobutyraldehyde;  $P(\text{O}_2) = 1$  atm, room temp. (ca. 20°C),  $[\text{Cu}^{\text{II}}] = 2$  mM,  $[\text{aldehyde}] = 0.7$  M

Entry	Catalyst	[olefin]	Conv. (%)	Sel. (%)	Time (h)	Colour <sup>a</sup>
1	<b>1</b>	0.15	100	83	20	deep blue
2	<b>1</b>	0.28	84	99	24	deep blue
3	<b>P1</b>	0.27	58	78	24	deep blue
4	<b>2</b>	0.26	100	81	30	deep blue
5	<b>2</b>	0.26 <sup>b</sup>	none	–	30	pale blue
6	<b>2<sup>c</sup></b>	0.33	84	73	20	deep blue
7	<b>3</b>	0.27	92	85	30	emerald green
8	<b>1</b>	0.20 <sup>d</sup>	none	–	20	deep blue

<sup>a</sup> Reacting solution.

<sup>b</sup> No aldehyde.

<sup>c</sup>  $[\text{Cu}^{\text{II}}] = 0.2$  mM.

<sup>d</sup> Propionaldehyde diethyl acetal as solvent and sacrificial reductant.

Remarkable catalytic activity and selectivity are observed also for poly- $\text{Cu}(\text{aaema})_2$  (**P1**), but evident metal leaching is observed.

All copper(II) complexes exhibit both catalytic activity and selectivity comparable with those of the best Mukaiyama's  $\text{Ni}^{\text{II}}$  catalyst, i.e.  $\text{Ni}(\text{dpm})_2$  (dpm = dipivaloylmethanate) [1b]. In one case (entry 2) almost 100% selectivity is observed, a feature which makes this catalyst extremely promising for potential applications. Remarkably, the

coordination sphere of copper(II) does not seem to strongly affect both activity and selectivity of the metal center. Comparable selectivity is exhibited also by the homopolymer of **1** (**P1**, entry 3) but, in this case, a lower activity is observed. Moreover, metal leaching from the solid apparently occurs, as revealed by the colour of the liquid phase in the reaction mixtures. It is not clear yet if the relatively low activity of **P1** is related to this circumstance.

The data reported herein confirm that also with these copper(II)-based catalysts the sacrificial reductant is necessary for catalytic activity (see entry 5). In this connection, acetals do not seem to be useful (see entry 8), in contrast with Mukaiyama's observations in the Co<sup>II</sup> catalyzed systems [4].

We are planning to investigate on the mechanism of the epoxidation reaction on the basis of an electrochemical approach [5].

## Acknowledgements

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## References

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