

Catalytic oxidation of tetrahydrofuran in the presence of 14-membered hexaaza macrocyclic Copper (II) complexes with hydrogenperoxide

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Copper (II) Complexes of the 14-membered hexaaza-macrocycles; 1, 8-dimethyl-; 1, 8-diethyl-; 1, 8-dipropyl-; 1, 8-dibutyl^{iso}-; 1, 8-dibutyl^{sec}- and 1, 8-dibenzyl- 1, 3, 6, 8, 10, 13-hexaazacyclotetra decane ([Cu{R₂[14]aneN₆}(ClO₄)₂)] catalysed efficiently the selective oxidation of tetrahydrofuran into the corresponding γ -butyrolactone and a small amount of tetrahydrofuran-2-ol and 4-hydroxybutyraldehyde, using dil. H₂O₂ as the oxidant. The conversion of this catalytic oxidation process can reach 98.6% when [Cu{(Benzyl)₂[14]ane N₆}(ClO₄)₂] is used.

Keywords: hexaazamacrocyclic, oxidation, tetrahydrofuran, copper

One of the major current challenges in synthetic organic chemistry is the selective oxidation of organic compounds using O₂, TBHP, H₂O₂ and PhIO as oxygen donors in the presence of transition metal catalysts.¹ The selective oxidative functionalisation at the α C–H bond of ethers is one of the most useful reactions in organic synthesis, because it provides for the efficient preparation of esters (or lactones in the case of cyclic ethers).² Such conversions are usually accomplished by the use of either stoichiometric amounts of CrO₃, Pb (CH₃COO)₄, and RuO₃ as oxidants,^{3,4} or catalytic amounts of RuO₄ in the presence of OCl⁻ or IO₄.⁵ Most recently, several new oxidation systems have been described using transition metal complexes for the transformation of ethers to esters,⁶ tetrahydrofuran was also oxidised to the corresponding hydroxy-aldehyde with Co(II) porphyrin by employing a combination of dioxygen and 2-methylpropanal.⁷ Furthermore, Sudalai *et al.* have been reported that titanium silicates (TS-1, TS-2) catalysed efficiently the selective oxidation of tetrahydrofuran with H₂O₂ as the oxidant to γ -Butyrolactone.⁸ In our recent publications, we reported the role of some transition metals and their complexes included within zeolite Y as catalysts.^{9–11} In both cases, it was observed that these catalysts were able to transfer oxygen from TBHP and H₂O₂ to substrate and hydroxylate the hydrocarbons. Recently, we found that air-stable iron (III) and manganese (II) bipyridine complexes included in zeolite Y and bentonite can easily catalyse the oxidation of tetrahydrofuran (THF) under H₂O₂ and TBHP as oxidant to give tetrahydrofuran-2-ol, tetrahydrofuran-2-one with minor amounts of 2,3-dihydrotetrahydrofuran.¹⁰ In this study we synthesised several Cu (II) complexes with ligands of 14-membered hexaaza macrocycles and find that they catalyse the oxidation of tetrahydrofuran with hydrogen peroxide.

In a typical procedure, a mixture of catalyst (0.2 g) and tetrahydrofuran (10 ml) was stirred in a 50 ml round bottom two-necked flask equipped with a condenser and dropping funnel for 30 min, under nitrogen atmosphere. Then 8 ml of the hydrogenperoxide (30% in H₂O) was added through the dropping funnel. The mixture was then refluxed for 8 h. The reaction mixture was analysed by GC and GC–MS. The product yields were determined by GC analysis using naphthalene as internal standard. The solvent was removed under reduced pressure and the residue purified by chromatography to give γ -butyrolactone (**1**), which was further confirmed by ¹H NMR analysis, a small amount of the corresponding tetrahydrofuran-

Table 1 Substrate conversions and product selectivities in the oxidation of tetrahydrofuran with H₂O₂ in the presence of 14-membered hexaaza macrocyclic copper (II) complexes

Catalyst	Conversion /%	Yield/%		
		1	2	3
[Cu{[14]ane N ₆ }(ClO ₄) ₂]	54.2	68.7	18.4	12.9
[Cu{(CH ₃) ₂ [14]ane N ₆ }(ClO ₄) ₂]	58.6	76.5	16.7	6.8
[Cu{(C ₂ H ₅) ₂ [14]ane N ₆ }(ClO ₄) ₂]	61.4	81.6	13.6	4.8
[Cu{(butyl ^{iso}) ₂ [14]ane N ₆ }(ClO ₄) ₂]	71.5	84.3	10.5	5.2
[Cu{(butyl ^{sec}) ₂ [14]ane N ₆ }(ClO ₄) ₂]	72.3	88.4	6.7	4.9
[Cu{(benzyl) ₂ [14]ane N ₆ }(ClO ₄) ₂]	98.6	100	-	-

2-ol (**2**) and 4-hydroxybutyraldehyde (**3**) (Scheme 1). All catalysts were also examined under the same reaction conditions and their conversions and selectivity are summarised in Table 1. It is clear that the conversion highly depends on the solubility of the catalyst used in THF, that is the homogeneous reaction phase gave a higher conversion. Soluble 1,9-dibenzyl-1, 3, 7, 9, 11, 15-hexaazacyclo hexadecane copper (II) in THF usually give a high conversion, but [Cu {(CH₃)₂[14]ane N₆}]²⁺ and [Cu {[14]ane N₆}]²⁺ catalysts only give a low conversion.

Experimental

All the materials were of commercial reagent grade. Tetrahydrofuran was purified by standard procedures.¹² Melting points were obtained with a Yanagimoto micro melting point apparatus and are uncorrected. Gas chromatographic analyses of products were performed on a Philips, Pu-4400 chromatograph, 1.5 m, 3% OV-17 column and GC-MS (Varian 3400 chromatograph, 25m CBP-5 column coupled with a QP 1100EX MAT INCOF 50, 70ev). ¹H NMR spectra were determined for solution in CDCl₃ with tetramethylsilane as internal standard on a Bruker AC 80. All the solid compounds reported in this paper gave satisfactory C, H, N microanalyses with a Perkin-Elmer Model 240 analyzer. The 1, 8-dimethyl-, and 1, 8-diethyl-1, 3, 6, 8, 10, 13-hexaaza cyclotetradecane copper (II) complex were prepared according to the literature.¹³

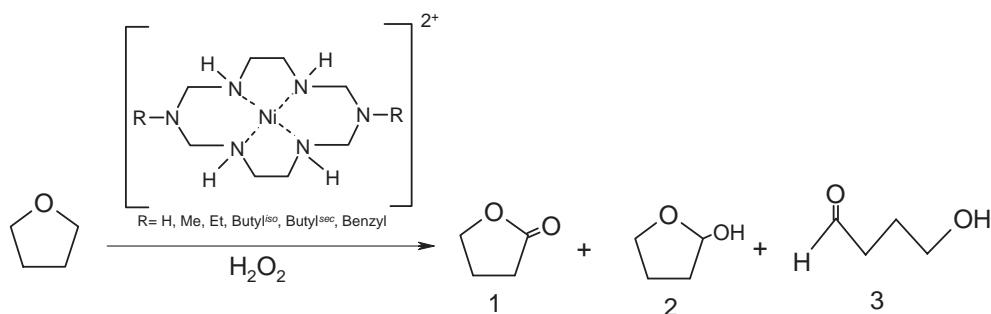
Synthesis

Caution: Some of compounds containing perchlorate anions must be regarded as potentially explosive and should be handled with caution.

1, 8-dipropyl, 1, 8-dibutyl^{iso}-; 1, 8-dibutyl^{sec}- and 1, 8-dibenzyl- 1, 3, 6, 8, 10, 13-hexaazacyclotetradecane copper (II) perchlorate were synthesised according to the following procedures.¹³ To a stirred methanol solution (75 ml) of CuCl₂ · 2H₂O (4 g, 23 mmol) were slowly added 99% ethylenediamine (2.82 g, 47 mmol), 36% formaldehyde (9.4 ml) and R-NH₂ (R= *pr*, butyl^{iso}, butyl^{sec}, benzyl) (46 mmol). The mixture was heated at reflux for 24 h until a deep blue-violet solution resulted. The solution was cooled to room temperature and filtered to remove

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† This is a Short Paper, there is therefore no corresponding material in *J Chem. Research (M)*.



Scheme 1

copper hydroxide. Excess perchloric acid or lithium perchlorate dissolved in methanol was added to the filtrate, and the mixture was kept in the refrigerator until purple-red crystals formed. The crystals were filtered, washed with methanol, and air dried. The crystals were recrystallised from hot water.

[Cu{(pr)₂[14]ane N₆}(ClO₄)₂]: Yield: ~ 35 %. Anal. Calcd for CuC₁₄H₃₄N₆Cl₂O₈: Cu, 11.58; C, 30.63; H, 6.24; N, 15.31. Found: Cu, 11.49; C, 30.51; H, 6.13; N, 15.42 %. IR (KBr): 3214 cm⁻¹ (ν_{N-H}). UV-Vis (CH₃NO₂): 496 nm (ε = 80 M⁻¹ cm⁻¹)

[Cu{(butyl^{iso})₂[14]ane N₆}(ClO₄)₂]: Yield: ~ 46%. Anal. Calcd for CuC₁₆H₃₈N₆Cl₂O₈: Cu, 11.01; C, 33.31; H, 6.64; N, 14.57. Found: Cu, 10.92; C, 33.21; H, 6.53; N, 14.63 %. IR (KBr): 3228 cm⁻¹ (ν_{N-H}). UV-Vis (CH₃NO₂): 487 nm (ε = 79 M⁻¹ cm⁻¹)

[Cu{(Benzyl)₂[14]ane N₆}(ClO₄)₂]: Yield: ~ 59 %. Anal. Calcd for CuC₂₂H₃₄N₆Cl₂O₈: Cu, 9.85; C, 40.97; H, 5.31; N, 13.03. Found: Cu, 9.79; C, 40.86; H, 5.27; N, 13.17 %. IR (KBr): 3234 cm⁻¹ (ν_{N-H}). UV-Vis (CH₃NO₂): 491 nm (ε = 83 M⁻¹ cm⁻¹)

γ-Butyrolactone: ν_H (CDCl₃) 2.26 (2H, q, J 6.6, CH₂), 2.46 (2H, t, J 7.0, CH₂) and 4.32 (2H, t, J 6.9 Hz, CH₂).

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