

Organotin-oxomolybdate coordination polymers as catalysts for the epoxidation of cyclooctene

Marta Abrantes^a, Anabela A. Valente^b, Isabel S. Gonçalves^{b,*},
Martyn Pillinger^b, Carlos C. Romão^a

^a Instituto de Tecnologia Química e Biológica da Universidade Nova de Lisboa, Quinta do Marquês, EAN,
Apt. 127, 2781-901 Oeiras, Portugal

^b Department of Chemistry, CICECO, University of Aveiro, Campus de Santiago, 3810-193 Aveiro, Portugal

Received 12 November 2004; received in revised form 7 April 2005; accepted 3 May 2005

Available online 13 June 2005

Abstract

The organotin-oxomolybdate coordination polymers $[(R_3Sn)_2MoO_4] \cdot nH_2O$ (R = methyl, *n*-butyl, cyclohexyl, phenyl, benzyl) were tested as catalysts for the liquid-phase epoxidation of cyclooctene with 30% aqueous hydrogen peroxide at 35 °C and atmospheric pressure. Water, acetonitrile and dichloromethane were examined as additional co-solvents for the reaction. The catalytic results vary considerably with the nature of the tin-bound R group and the co-solvent. For all systems, cyclooctene oxide was the only observed reaction product. Apart from the trimethyltin derivative, the best results were obtained without additional co-solvent or with CH_2Cl_2 , while addition of water or CH_3CN had a detrimental effect on catalytic performance. The highest turnover frequency ($46 \text{ mol mol}_{Mo}^{-1} \text{ h}^{-1}$) was obtained for the system containing the tri-*n*-butyltin derivative as catalyst and CH_2Cl_2 as solvent. Complete conversion of the substrate was achieved for this system within 4 h. Using water instead of CH_2Cl_2 with the *n*-butyl catalyst reduced the catalytic activity considerably at the beginning of the reaction, although 91% conversion was achieved after 24 h. The behavior of the trimethyltin derivative was atypical in that conversion of cyclooctene was only possible when CH_3CN was used as the co-solvent. Experiments were also carried out using a urea/hydrogen peroxide adduct as a water-free source of H_2O_2 . However, the catalytic activities observed were significantly lower than those obtained using aqueous H_2O_2 .

© 2004 Elsevier B.V. All rights reserved.

Keywords: Molybdenum; Tin; Coordination polymer; Epoxidation; Cyclooctene; Hydrogen peroxide

1. Introduction

Epoxides are important organic intermediates because they undergo ring-opening reactions with a variety of reagents to give mono- or bi-functional organic products [1]. In general, epoxides can be prepared by the reaction of olefins with hydrogen peroxide or alkylhydroperoxides, catalyzed by high-valent early transition-metal compounds [2]. Recently, we reported that organotin-oxometalate coordination polymers, formulated as $[(nBu_3Sn)_2MO_4]$ (M = Mo or W), exhibit good catalytic activity and selectivity for the

epoxidation of olefins using either *tert*-butyl hydroperoxide (in decane) or 30% aqueous H_2O_2 as the oxidant [3]. For the model substrate cyclooctene, the best results were obtained using the molybdenum(VI) compound as catalyst, aqueous H_2O_2 as oxidant and dichloromethane as co-solvent. The tri-*n*-butyltin derivatives belong to a wider family of materials, reported by Fischer and co-workers in 1993 [4], having the general formula $[(R_3E)_2MO_4]$ [R = Me, Et, *n*Pr, *n*Bu and phenyl (Ph); E = Sn and Pb; M = Mo and W]. These compounds are interesting candidates as catalysts or catalyst precursors for oxidation reactions, but to the best of our knowledge their catalytic properties had not been investigated until our recent efforts [3,5]. The related polymeric organotin-oxorhenium compound $Me_3SnOReO_3$ was tested as a catalyst for aldehyde olefination, but found to be inactive

* Corresponding author. Tel.: +351 234 370200; fax: +351 234 370084.

E-mail addresses: igoncalves@dq.ua.pt (I.S. Gonçalves),
ccr@itqb.unl.pt (C.C. Romão).

[6,7]. After studying the tri-*n*-butyltin derivatives as epoxidation catalysts, we turned our attention to the oxidation of benzothiophene by aqueous H₂O₂ in the presence of the organotin-oxomolybdate family [(R₃Sn)₂MoO₄] [R = Me, *n*Bu, Ph, benzyl (Bz), cyclohexyl (Cy)] [5]. The catalytic results depend on the complex interplay between various factors, such as the addition of co-solvents and the nature and size of the tin-bound *R* groups. Cyclooctene epoxidation in the presence of the polymer [(*n*Bu₃Sn)₂MoO₄] was also found to depend on the type of co-solvent added [3], but the influence of the tin-bound *R* groups on catalytic performance was not explored due to the preliminary character of the study. In the present work, we have further examined the epoxidation activity of the organotin-oxomolybdate family in different solvents.

2. Experimental

2.1. Materials and methods

The oxidant urea hydrogen peroxide adduct (UHP) was obtained from Aldrich and used as received. Solvents were dried by standard procedures, distilled under nitrogen and stored over molecular sieves. The organotin-oxomolybdates **1–5**, formulated as [(R₃Sn)₂MoO₄]*n*H₂O with R = Me (**1**), *n*Bu (**2**), Cy (**3**), Ph (**4**) and Bz (**5**), were prepared as described previously by the addition of a saturated aqueous solution of Na₂MoO₄·2H₂O to a solution/suspension of R₃SnCl in either water (**1,2**) or acetone (**3–5**) at room temperature [3–5]. Microanalyses were performed at the ITQB (by Almeida). IR spectra were measured on a Mattson 7000 FT-IR spectrometer using KBr pellets. Powder X-ray diffraction (XRD) data were collected on a Philips X'pert diffractometer using Cu K α radiation filtered by Ni. The characterization data for compounds **1–5** were in agreement with published results [3–5].

2.2. Catalysis

Catalytic oxidation of *cis*-cyclooctene was performed under air (atmospheric pressure) in a reaction vessel equipped with a magnetic stirrer, immersed in a thermostated oil bath at 35 °C. A 1% molar ratio of catalyst/substrate (7.2 mmol cyclooctene and 72 μ mol catalyst **1–5**) and a hydrogen peroxide (30% aqueous or UHP)/cyclooctene molar ratio of 2 were used, with 3 mL solvent. The course of each reaction was monitored by GC-analysis using 800 mg *n*-dibutylether as internal standard. Samples were withdrawn periodically and diluted with dichloromethane. For the destruction of the peroxide and removal of water, a catalytic amount of manganese dioxide and dried magnesium sulfate were added. The resulting slurry was filtered over a Pasteur pipette filled with cotton and silica and the filtrate was injected in a Thermofinnigan Trace 2000 gas chromatograph equipped with a J&W capillary column (Cyclosilb, 30 m \times 0.25 mm \times 0.25 μ m) and a flame ionization detector.

3. Results and discussion

The epoxidation of *cis*-cyclooctene in the presence of compounds **1–5** was carried out using 30% aqueous hydrogen peroxide at 35 °C and atmospheric pressure. A molar ratio of substrate:oxidant:catalyst = 100:200:1 was used. Dichloromethane was chosen as a representative non-coordinating solvent, acetonitrile as a coordinating solvent and water as a “green” (and coordinating) solvent. Reactions were also performed in the absence of any additional co-solvent. The systems containing just water or water + CH₂Cl₂ are composed of two liquid layers (emulsified with magnetic stirring) because the substrate (cyclooctene) and the oxidant (aqueous H₂O₂) are not miscible. In contrast, a single liquid phase is obtained when CH₃CN is used as the co-solvent. The trimethyltin derivative [(Me₃Sn)₂MoO₄] (**1**) dissolves readily in the presence of either CH₃CN or CH₂Cl₂. Compound [(*n*Bu₃Sn)₂MoO₄] (**2**) only dissolves completely when CH₃CN is the co-solvent and [(Cy₃Sn)₂MoO₄] (**3**) when CH₂Cl₂ is the co-solvent. For all the other cases the polymers remain partially or totally insoluble in the catalytic system, thereby forming a biphasic or triphasic system. Control experiments showed that cyclooctene oxidation does not take place to a measurable extent in the absence of a catalyst, during 8 h. For all the catalytic tests cyclooctene epoxide was the only reaction product observed up to 24 h. With the exception of compound **1**, the turnover frequencies (TOF, calculated for the first 2 h of reaction) of cyclooctene conversion vary according to the type of co-solvent, generally increasing in the order water < CH₃CN < CH₂Cl₂ (Fig. 1). In accordance with previous results for benzothiophene oxidation, this trend parallels the decrease in solvent polarity, as indicated by the dielectric constants (ϵ) at 25 °C: water (80.10) > CH₃CN (35.94) > CH₂Cl₂ (8.93).

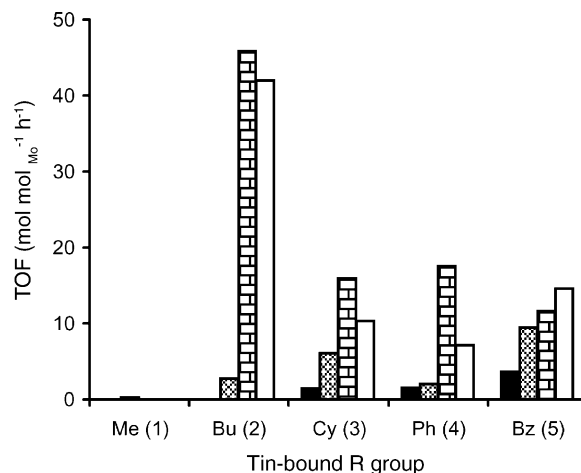


Fig. 1. Turnover frequencies of cyclooctene conversion with aqueous H₂O₂ at 35 °C (calculated for the first 2 h of reaction) in the presence of the organotin-oxomolybdates [(R₃Sn)₂MoO₄] (**1–5**) in water (solid bars), CH₃CN (diamonds), CH₂Cl₂ (bricks) and without additional co-solvent (open bars).

The trimethyltin derivative **1** does not follow the trends set by the other polymers and in fact no reaction was observed after 2 h for any of the solvent systems studied. The poor performance of **1**, in relation to the other organotin-oxomolybdates under study, was also noted previously for the oxidation of benzothiophene with H_2O_2 (in the presence of either water or water + 1,2-dichloroethane). Compound **1** has a layered structure built up of tetrahedral MoO_4 and trigonal-bipyramidal Me_3SnO_2 units [4]. One possible explanation for the atypical catalytic behavior of this compound with water as the co-solvent is that the diffusion of substrate and/or oxidant molecules between the layers of the solid catalyst could be hindered by the hydrophobic character of the interlamellar space. The tri-*n*-butyltin derivative **2** is also insoluble under these conditions but after 24 h 91% conversion was achieved. Although the crystal structure of **2** is as yet unknown, it is reasonable to assume that the bulkier *n*-butyl groups originate a more open structure, thereby facilitating eventual intercalation of reactant molecules. The trimethyltin derivative **1** dissolves completely when CH_2Cl_2 is the co-solvent. However, the system remains inactive, even after 24 h. Extended

X-ray absorption fine structure (EXAFS) studies for compounds **1–5** in the solid state showed that the connectivity of the $[\text{MoO}_4]^{2-}$ subunits and $[\text{R}_3\text{Sn}]^+$ spacers for compound **1** is subtly different from that for the other four coordination polymers [3,5]. The structural differences may be a contributory factor to the contrasting catalytic activities observed.

Fig. 2 shows the kinetic profiles for cyclooctene epoxidation in the presence of the organotin-oxomolybdates **1–5** and the different co-solvents. In the case of water and CH_3CN the kinetic profiles are quite similar for polymers **2–5**, showing that for each catalyst the reaction proceeds at lower rates than in the other solvent systems and initial induction periods occur, which are not observed for CH_2Cl_2 or without co-solvent. The addition of water or CH_3CN has a detrimental effect on the initial catalytic activity, especially for **2**. This negative effect may be related to the coordinating powers of the solvent molecules. According to the mechanisms proposed for H_2O_2 -based epoxidations of olefins with Mo^{VI} complexes, the competition between solvent and oxidant molecules for coordination to the metal center may retard the activation of the oxidant, which is necessary for subsequent

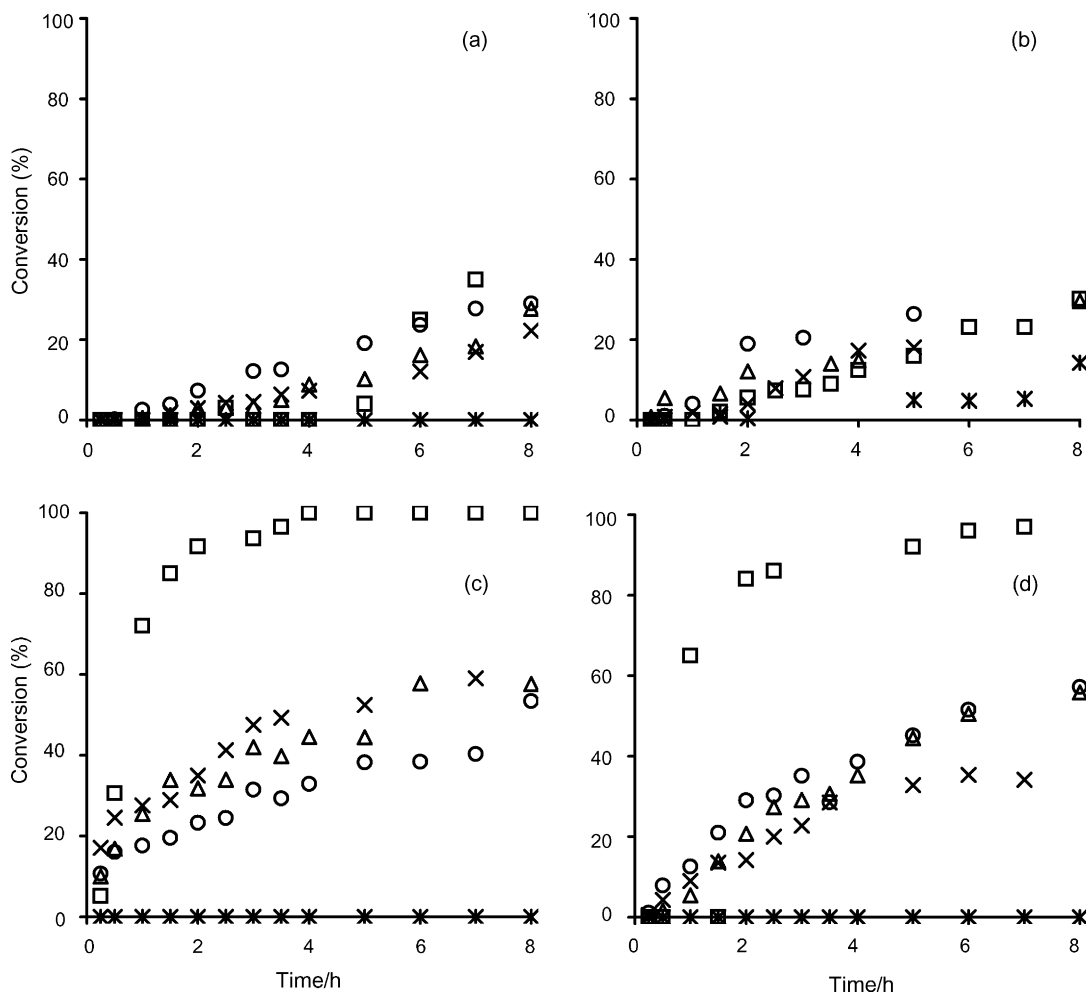


Fig. 2. Kinetics of cyclooctene epoxidation with aqueous H_2O_2 at 35°C in the presence of the organotin-oxomolybdates $[(\text{R}_3\text{Sn})_2\text{MoO}_4]$ [$\text{R} = \text{Me}$ (**1**) (*), Bu (**2**) (\square), Cy (**3**) (\triangle), Ph (**4**) (\times), Bz (**5**) (\circ)] with water (a), CH_3CN (b), CH_2Cl_2 (c) and without co-solvent (d). Molar ratio substrate:oxidant:catalyst = 100:200:1.

epoxidation of the substrate by nucleophilic attack on an electrophilic oxygen atom of the intermediate species [8,9]. The use of CH_2Cl_2 , a non-coordinating solvent, has a beneficial effect on catalytic performance for the polymers 2–4, especially in the case of the tri-*n*-butyltin derivative 2, which yields cyclooctene oxide quantitatively within 4 h at 35 °C. As reported previously [3], compound 2 also works very well with 1,2-dichloroethane as the co-solvent. For this system it was proven experimentally that the catalysis was almost exclusively heterogeneous in nature.

Fig. 3 shows the cyclooctene conversions obtained after 24 h of reaction. The tri-*n*-butyltin derivative 2 continues to be the best catalyst and gives the highest conversions in all the solvent systems. An interesting observation is that for compounds 2 and 5 with water as the co-solvent the cyclooctene conversions after 24 h (91 and 69%, respectively) are close to those obtained with either CH_2Cl_2 or without additional co-solvent (95–100 and 77–81%, respectively). Hence, for these compounds the solvent effect of water on the reaction rate is more pronounced during the first few hours of the reaction but loses importance as the reaction proceeds. For the polymers 3 and 4 the detrimental effect of water persists. From our previous characterization studies, it was determined that compounds 2 and 3 are anhydrous while 4 and 5 are hydrated. However, neither the initial reaction rates (based on TOF) nor the conversions after 24 h seem to correlate with the presence of water molecules in the polymer structure. Fig. 3 shows that significant conversion of cyclooctene in the presence of the trimethyltin derivative 1 only occurred in the presence of CH_3CN after 24 h. The formation of acetylperoxyimidic acid derived from the reaction of H_2O_2 with acetonitrile is possible and this reactive intermediate may function as an epoxidizing agent for cyclooctene conversion [10].

These results, taken together with our previous findings, suggest that water inhibits the catalytic activity (especially

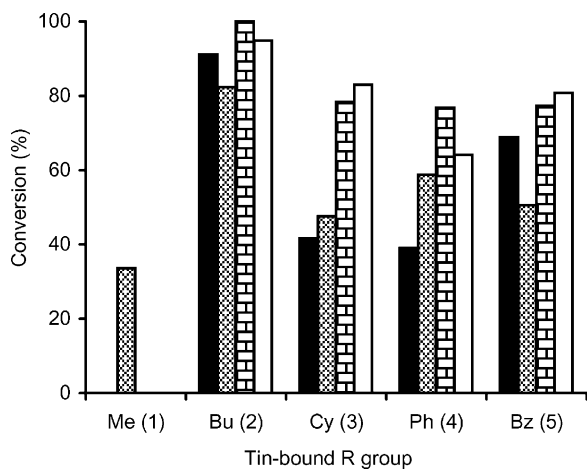


Fig. 3. Cyclooctene conversion after 24 h of reaction with aqueous H_2O_2 at 35 °C in the presence of the organotin-oxomolybdates $[(\text{R}_3\text{Sn})_2\text{MoO}_4]$ (1–5) in water (solid bars), CH_3CN (diamonds), CH_2Cl_2 (bricks) and without additional co-solvent (open bars).

at the beginning of the reaction) of this family of organotin-oxomolybdates. None of the systems described above are water free since an aqueous solution of H_2O_2 has been used. In order to study the catalytic performance of $[(\text{Bu}_3\text{Sn})_2\text{MoO}_4]$ (2) in the absence of water, experiments were performed using a urea/hydrogen peroxide (UHP) adduct as the oxidant. The UHP adduct has the additional advantages of being safer and easier to handle than 30% aqueous H_2O_2 [11]. It has successfully been used in metal mediated olefin epoxidation with methyltrioxorhenium [12,13], Mn (porphyrins) [14], titanium silicates [15,16] and Keggin-type polyoxometalates [17]. Unfortunately, the reaction carried out with UHP and CH_2Cl_2 as solvent was rather sluggish, yielding 10% epoxide after 24 h compared to 100% obtained within 4 h when aqueous H_2O_2 was used (Fig. 4). The dissociation of UHP is necessary to liberate H_2O_2 for the catalytic reaction and occurs until equilibrium is reached. Possibly, under the applied conditions the dissociation of the UHP adduct is very slow. It has been reported that catalytic amounts of water tend to speed up the approach to the equilibrium [14]. Experiments carried out with 0.8 molar ratio of $\text{H}_2\text{O}/\text{UHP}$ in CH_2Cl_2 showed some improvement in the catalytic activity of compound 2 (Fig. 4), but the reaction was still much slower than that observed with aqueous H_2O_2 , yielding only 15% epoxide after 24 h. The UHP adduct was also tested as the oxidant without additional solvent or with CH_3CN . For each system, the catalytic performance of 2 was poorer than that observed with aqueous H_2O_2 (compare Figs. 2 and 4 through 8 h). Conversion at 24 h was still much lower for the UHP systems. The poor results obtained with UHP may be due to the fact that this H_2O_2 adduct does not dissolve completely in any of the above solvent systems.

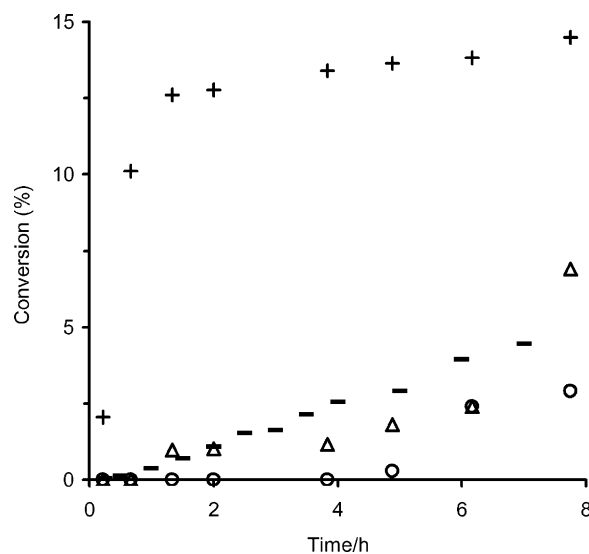


Fig. 4. Kinetics of cyclooctene oxidation at 35 °C in the presence of the organotin-oxomolybdate $[(\text{Bu}_3\text{Sn})_2\text{MoO}_4]$ (2) using CH_2Cl_2 -UHP (—), CH_2Cl_2 -UHP-water (+), CH_3CN -UHP-water (Δ) and UHP-water (\circ). Molar ratio substrate:oxidant:catalyst = 100:200:1.

4. Conclusion

In this work, coordination polymers with the general formula $[(R_3Sn)_2MoO_4] \cdot nH_2O$ ($R = Me, nBu, Cy, Ph, Bz$) have been tested as catalysts for the epoxidation of cyclooctene at 35 °C. The results depend on the addition of co-solvents and the nature of the tin-bound R groups. The best system is obtained using the tri- n -butyltin derivative as catalyst, aqueous H_2O_2 as oxidant and dichloromethane as solvent. Using this catalyst and water as solvent it is also possible to obtain quite satisfactory conversions, although delayed in time. Performing the reaction in a water-free environment using a urea/hydrogen peroxide adduct as the oxidant did not accelerate the catalytic performance of the n -butyl derivative. In the future, we intend to further explore the catalytic activity of these compounds for the epoxidation of other substrates. More detailed structural investigations are also needed if the contrasting catalytic behaviors are to be understood. We are also interested in building chiral coordination polymers to be tested in enantioselective catalysis.

Acknowledgments

This work was partly funded by the FCT, POCTI and FEDER. (Including a Ph.D. grant to MA and project POCTI/QUI/37990/2001).

References

- [1] J.W. Schwesinger, T. Bauer, in: G. Helmchen, R.W. Hoffmann, J. Mulzer, E. Schaumann (Eds.), *Stereoselective Synthesis*, vol. E21e, Houben Weyl Thieme, New York, 1995, pp. 4599–4648.
- [2] K.A. Jorgensen, *Chem. Rev.* 89 (1989) 431.
- [3] M. Abrantes, A.A. Valente, M. Pillinger, I.S. Gonçalves, J. Rocha, C.C. Romão, *J. Catal.* 209 (2002) 237.
- [4] U. Behrens, A.K. Brimah, K. Yünlü, R.D. Fischer, *Angew. Chem. Int. Ed. Engl.* 32 (1993) 82.
- [5] M. Abrantes, A.A. Valente, M. Pillinger, I.S. Gonçalves, J. Rocha, C.C. Romão, *Chem. Eur. J.* 9 (2003) 2685.
- [6] F.E. Kühn, A. Scherbaum, W.A. Herrmann, *J. Organomet. Chem.* 689 (2004) 4149.
- [7] C.C. Romão, F.E. Kühn, W.A. Herrmann, *Chem. Rev.* 97 (1997) 3197.
- [8] V. Hulea, P. Moreau, *J. Mol. Catal.* 113 (1996) 499.
- [9] O. Bortolini, S. Campestrini, F. Di Furia, G. Modena, *J. Org. Chem.* 52 (1987) 5093.
- [10] G.B. Payne, P.H. Deming, P.H. Williams, *J. Org. Chem.* 26 (1961) 659.
- [11] M.S. Cooper, H. Heaney, A.J. Newbold, W.R. Sanderson, *Synlett* 9 (1990) 533.
- [12] W. Adam, C.M. Mitchell, *Angew. Chem. Int. Ed. Engl.* 35 (1996) 533.
- [13] H. Tan, J.H. Espenson, *Inorg. Chem.* 37 (1998) 467.
- [14] A.M.R. Gonsalves, R.A.W. Johnstone, M.M. Pereira, *J. Chem. Soc., Perkin Trans.* (1991) 645.
- [15] W. Adam, R. Kumar, T.I. Reddy, M. Renz, *Angew. Chem. Int. Ed. Engl.* 35 (1996) 880.
- [16] S.C. Laha, R. Kumar, *J. Catal.* 208 (2002) 339.
- [17] Y. Ding, Q. Gao, G. Li, H. Zhang, J. Wang, L. Yan, J. Suo, *J. Mol. Catal. A: Chem.* 218 (2004) 161.