



Communication

Ring-opening of epoxides promoted by organomolybdenum complexes of the type $[(\eta^5\text{-C}_5\text{H}_4\text{R})\text{Mo}(\text{CO})_2(\eta^3\text{-C}_3\text{H}_5)]$ and $[(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_3(\text{CH}_2\text{R})]$



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ABSTRACT

The cyclopentadienyl molybdenum carbonyl complexes $[(\eta^5\text{-C}_5\text{H}_4\text{R})\text{Mo}(\text{CO})_2(\eta^3\text{-C}_3\text{H}_5)]$ and $[(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_3(\text{CH}_2\text{R})]$ ($\text{R} = \text{H}, \text{COOH}$) have been shown to promote acid-catalysed reactions in liquid phase, under moderate conditions. The catalytic alcoholysis of styrene oxide with ethanol at 35 °C gave 2-ethoxy-2-phenylethanol in 100% yield within 30 min for the dicarbonyl complexes and 3–6 h for the tricarbonyl complexes. Steady catalytic performances were observed in consecutive runs with the same catalytic solution, suggesting fairly good catalytic stability. In the second acid-catalysed reaction studied, the isomerization of α -pinene oxide at 55 °C gave campholenic aldehyde and *trans*-carveol in a total yield of up to 86% at 100% conversion. Chemoselectivity is shown to be solvent dependent.

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1. Introduction

Epoxides are important organic intermediates, commonly synthesized from olefins, with patented technologies including the use of homogeneous Mo^{VI} catalysts, such as those derived from molybdenum carbonyl catalyst precursors [1–3]. Epoxides can undergo ring-opening reactions in the presence of acid catalysts to give a plethora of useful intermediates and products for the fine chemicals industry [4–6]. Commonly used Lewis acid catalysts such as metal halide salts present numerous drawbacks such as corrosion problems, fast deactivation, the production of large volumes of acidic waste, and the need for high catalyst/substrate ratios. Hence, there is much interest in the development of novel reaction processes catalysed by highly active and highly selective Lewis acids that significantly reduce acidic wastes. The use of organometallic Lewis acids (OLAs) is promising since they are playing an increasingly important role in modern organic synthesis

due to the high product selectivities often reachable together with straightforward catalyst optimization through ligand exchange and/or functionalization [7].

Several group 6 (Mo, W) metal carbonyl complexes are OLAs [8] and have been used in a series of acid-catalysed reactions [9–15]. Molybdenum-based catalysts are especially attractive due to the ready availability and low cost of this element. We recently started to explore organomolybdenum complexes for the catalytic isomerization of α -pinene oxide (PinOx) to campholenic aldehyde (CPA). This is an important reaction from two perspectives. Firstly, PinOx is a renewable chemical obtained from α -pinene, which is produced on an industrial scale either by tapping trees (gum turpentine) or as a byproduct of paper pulping. Secondly, CPA is useful as an aroma chemical and as a synthetic intermediate for other aroma chemicals and also for some pharmaceuticals. In particular, it is used for the manufacture of sandalwood-like fragrances [16]. The isomerization of PinOx to CPA tends to be promoted by Lewis acid catalysts, while Brønsted acids give a mixture of compounds in low yields, such as *trans*-carveol (TCV), *trans*-sobrerol, and *p*-cymene. Apart from being expensive ingredients in the flavour industry (e.g., TCV is a constituent of the Valencia orange essence oil), these compounds

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have attracted interest due to their biological activities [17–19]. We obtained encouraging results for the isomerization of PinOx to CPA in the presence of the indenyl allyl dicarbonyl derivative $[(\eta^5\text{-Ind})\text{Mo}(\text{CO})_2(\eta^3\text{-C}_3\text{H}_5)]$ [20]: 56% CPA yield at 97% PinOx conversion, 3 h reaction at 35 °C. In a second investigation [21], even better performance was obtained using the dimeric complex $[(\eta^5\text{-Ind})\text{Mo}(\text{CO})_2(\mu\text{-Cl})_2]$: 67% CPA yield at 100% PinOx conversion, 30 min reaction at 35 °C. The latter result is roughly comparable to those reported for the salts ZnCl_2 and ZnBr_2 [22], used as catalysts in patented technology for the production of CPA [23,24].

Another chemical route for the valorization of epoxides involves ring-opening via alcoholysis to give β -alkoxy alcohol products [25], which are important precursors for a broad range of pharmaceuticals [26]. These reactions can be promoted by Lewis acid catalysts [27,28], for which molybdenum carbonyl complexes are interesting candidates.

In this work, we set out to explore the catalytic potential of cyclopentadienyl molybdenum carbonyl complexes of the type $[(\eta^5\text{-C}_5\text{H}_4\text{R})\text{Mo}(\text{CO})_2(\eta^3\text{-C}_3\text{H}_5)]$ and $[(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_3(\text{CH}_2\text{R})]$ ($\text{R} = \text{H}$ or COOH) for acid-catalysed ring-opening reactions of epoxides, namely the isomerization of PinOx, and alcoholysis of styrene oxide (StyOx) with ethanol, under mild reaction conditions (Fig. 1). To the best of our knowledge, this is the first report on the catalytic performance of metal carbonyl complexes in the alcoholysis of StyOx.

2. Experimental

2.1. Materials and methods

Transmission FT-IR spectra (KBr pellets) were measured on a Mattson 7000 FT-IR spectrometer with 4 cm^{-1} resolution. Styrene oxide (StyOx, > 97%, Fluka), α -pinene oxide (PinOx, > 95%, TCI), 1,2-dichloroethane (DCE, 99%, Aldrich), toluene ($\geq 99.9\%$, Aldrich) and absolute ethanol (EtOH, 99.8%, Scharlau) were purchased from commercial sources and used as received.

2.2. Synthesis of molybdenum carbonyl complexes 1–4

The π -allyl complex $[\text{CpMo}(\text{CO})_2(\eta^3\text{-C}_3\text{H}_5)]$ (**1**) ($\text{Cp} = \eta^5\text{-C}_5\text{H}_5$) was synthesized according to the general procedure described

previously by Ascenso et al. [29], involving the reaction of $[(\eta^3\text{-C}_3\text{H}_5)\text{Mo}(\text{CO})_2(\text{NCCH}_3)_2\text{Cl}]$ with LiCp . The acid $[(\eta^5\text{-C}_5\text{H}_4\text{COOH})\text{Mo}(\text{CO})_2(\eta^3\text{-C}_3\text{H}_5)]$ (**2**) was obtained from the reaction of **1** with $n\text{-BuLi}$ and solid CO_2 , followed by aqueous work-up [30,31]. The tricarbonyl complex $[\text{CpMo}(\text{CO})_3\text{CH}_3]$ (**3**) was synthesized by the reaction of $[\text{CpMo}(\text{CO})_3]\text{Na}$ with CH_3I [32]. The reaction of NaCp with $\text{Mo}(\text{CO})_6$, followed by addition of 2-chloroacetamide, gave the complex $[\text{CpMo}(\text{CO})_3\text{CH}_2\text{COONH}_2]$, which was subsequently hydrolysed to give $[\text{CpMo}(\text{CO})_3\text{CH}_2\text{COOH}]$ (**4**) [33].

2.3. Catalytic tests

The catalytic reactions were carried out under air in a magnetically stirred, closed borosilicate reaction vessel (10 mL capacity) which was immersed in an oil bath thermostatted at 35 or 55 °C. Typically, the reactor was loaded with molybdenum complex, substrate (StyOx or PinOx) and a solvent. For the StyOx alcoholysis reaction, the reactor was loaded with molybdenum complex (80 μmol), StyOx (0.82 mmol), and ethanol (2.0 mL). For the PinOx isomerization reaction, the reactor was loaded with molybdenum complex (17 μmol), PinOx (170 μmol), and a solvent (0.5 mL; DCE, toluene or ethanol). The reactor containing the complex and the solvent was pre-heated for 10 min at the reaction temperature, and subsequently the substrate (also pre-heated) was added to the mixture (the reaction time was counted from this instant). The evolutions of the reactions were monitored using a Varian 3800 GC equipped with a BR-5 (Bruker) capillary column (30 m \times 0.25 mm; 0.25 μm) and a flame ionization detector, using H_2 as the carrier gas. Cyclododecane epoxide was used as an internal standard. The products were identified by GC–MS (Trace GC 2000 Series (Thermo Quest CE Instruments) – DSI II (Thermo Scientific)), equipped with a capillary DB-5 type column (30 m \times 0.25 mm; 0.25 μm), using He as the carrier gas.

3. Results and discussion

3.1. Styrene oxide ring-opening reaction via alcoholysis

Complexes **1–4** were explored for the acid-catalysed ring-opening reaction of StyOx with ethanol (also used as solvent) in the temperature range of 35–55 °C. All four complexes are completely

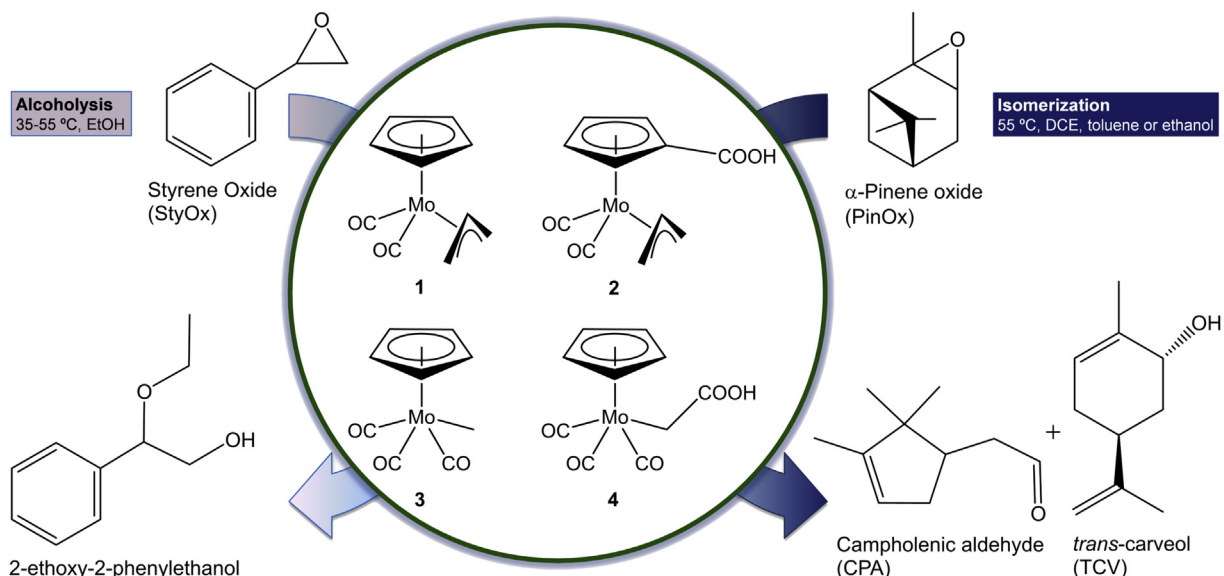


Fig. 1. Acid-catalysed epoxide ring-opening reactions studied in this work.

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