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Journal of Molecular Catalysis A: Chemical



journal homepage: www.elsevier.com/locate/molcata

Ruthenium (II) sulfoxides-catalyzed hydrogenolysis of glycols and epoxides

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ARTICLE INFO

Article history: Received 30 April 2012 Received in revised form 17 July 2012 Accepted 22 July 2012 Available online 31 July 2012

Keywords: Ruthenium catalysis Hydrogenolysis Glycols Epoxides

ABSTRACT

New selective deoxygenation reactions are needed for the efficient conversion of biomass-derived oxygenates to useful chemicals, including fuels. A new catalytic system is reported here for the selective hydrogenolysis of glycols to hydrocarbons. We find that *cis*-[RuCl₂(sulfoxide)₄] {sulfoxides: TMSO = tetramethylene sulfoxide; DMSO = dimethyl sulfoxide} catalyze the hydrogenolysis of glycols to alcohols and hydrocarbons by molecular hydrogen at 190–200 °C and 6.8–26 atm; the product yields range from moderate to excellent. The acid generated by catalysts in situ serves the purpose of dehydration step, hence added Bronstead acid as co-catalyst is not a prerequisite. Under similar conditions epoxides are converted primarily to mono-alcohols and hydrocarbons.

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1. Introduction

The search for new, efficient processes for the conversion of reduced oxygen-content products from renewable resources to value-added chemicals and fuels has stimulated new interest in the discovery of selective chemical transformation of biomassderived carbohydrates and polyols [1–4]. Metal-catalyzed biomass conversion to fuels and organic chemicals is vital to efficiently use ample, renewable resources [2–6]. Metal-catalyzed deoxygenation of glycol and epoxides are less developed than the epoxidation and dihydroxylation of alkenes which is extensively applied in organic synthesis and industry [7–9]. The use of biomass substantially reduces net carbon dioxide emissions because the latter is recycled in biomass production. Stoichiometric methods for the deoxydehydration of diols are abundant [10,11] but catalytic methods are limited [12–16]. Hydrogenolysis of polyols by various heterogeneous catalytic systems has been recently reported [17,18]. Bullock and Fagan found that $\{[Cp^*Ru(CO)_2]_2(\mu-H)\}^+OTf^-$ is a precursor for the selective hydrogenolysis of 1,2-propanediol to 1-propanol (Scheme 1) [19-21]. The total deoxygenation of glycerol and 1,2hexanediol to saturated hydrocarbons by [LRu(H₂O)_x(diimine)]²⁺ and [Cp*Ru(OH₂)(N–N)]⁺ was reported by Schlaf and coworkers [22,23].

Removal of two adjacent hydroxyl groups in a polyol by deoxydehydration (DODH) is a new attractive process for producing

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unsaturated and saturated hydrocarbons (Scheme 1). Several multi-step stoichiometric methods for glycol DODH are known [17,18], but one step [19-21] and catalytic methods are few and the latter are almost entirely based on oxo-rhenium complexes. The Bergman group reported the efficient conversion of polyols to olefins by formic acid at high temperature [24]. The potential of catalyzing DODH reactions by oxo-metal complexes (Cp*ReO₃) was demonstrated by Andrews and Cook [12] in the presence of PPh₃ as reductant. Gable and coworkers, with the help of experimental and computational studies, provided mechanistic insight of the reaction involving LReO₃ complexes as catalysts, especially the olefin-producing metallo-glycolate fragmentation step [25-30]. Abu-Omar et al. recently [13] achieved deoxygenation of epoxides and deoxydehydration of glycols to alkenes and alkanes using MeReO₃ as catalyst with the more practical reductant H₂. The Nicholas group [15] has demonstrated sulfite-driven DODH catalyzed by Me₃ReO₃ and Z⁺ReO₄⁻ and examined its scope and catalytic pathway under moderately mild reaction conditions. More recently the Bergman group [31] used rhenium-carbonyl as a pre-catalyst for the deoxydehydration of glycols to olefins using secondary alcohols as reducing agents.

The efficacy of ruthenium catalysts in hydrogenation and hydrogenolysis reactions is well established by us and others [32,33]. This prompted us to study the readily available and inexpensive catalysts for deoxydehydration with the more practical reductant H_2 . Molecular hydrogen is an attractive, robust, and inexpensive reductant due to its strong reducing potential and the production of environmentally benign water as a byproduct. In

^{1381-1169/\$ -} see front matter © 2012 Elsevier B.V. All rights reserved. http://dx.doi.org/10.1016/j.molcata.2012.07.025



Scheme 1. Metal hydrides or metal oxides catalyzed deoxygenation of glycols.

this report we reveal the first examples of selective conversion of glycols and epoxides to hydrocarbons and alcohols catalyzed by $RuCl_2(sulfoxide)_4$ **1a,b**. The catalysts, *cis*-[$RuCl_2(TMSO)_4$] (**1a**) (TMSO = tetramethylene sulfoxide) and *cis*-[$RuCl_2(DMSO)_4$] (**1b**), are easily prepared by the reaction of hydrated $RuCl_3$ with the respective sulfoxides [34,35].

2. Results and discussion

We started our investigation using 2-phenyl-1,2-ethanediol as a model glycol substrate (Scheme 2, R = Ph) and *cis*-[RuCl₂(TMSO)₄] (**1a**) or *cis*-[RuCl₂(DMSO)₄] (**1b**) as pre-catalysts. The reaction between the glycol and H₂ (6.8 atm) with 10 mol% **1a** or **1b** was conducted in benzene in a Parr steel autoclave at 190 °C. The GC and GC–MS analysis of the reaction mixture indicated the selective formation of 2-phenethyl alcohol (83% yields) and a small amount of phenyl acetaldehyde after 8 h (entry 1, Table 1). We also examined the reaction in the absence of catalyst under the similar reaction condition, only a trace amount of aldehyde was detected.

We extended the hydrogenolysis reactions promoted by **1a** to representative aliphatic glycols, better models for carbohydratederived polyols, to determine the products, selectivity and efficiency (Table 1). When 1,2-hexanediol was subjected to optimized reaction conditions (190°C, 6.8 atm H₂, 10 mol% **1a**) hexane was produced in 58% yield after 8h (entry 2) as the only detected product; at 120°C hexane was still produced exclusively in 62% yield in 3h (entry 3). 1,2-Tetradecanediol, a long chain glycol, was less reactive, and no hydrocarbons were detected at 200 °C under 6.8 atm H₂ in 48 h. However, when the reaction was conducted at $200 \degree C$ with $26 \arg H_2$, tetradecane (36%), tetradecanol (9%) and tetradecanal (trace) were produced in 96 h (entry 4). In contrast, the cyclic glycol cis-1,2-cyclohexanediol was unreactive under these conditions. To validate the utility of the Ru-catalyzed deoxygenation of a biomass-derived glycol, we investigated the reaction of 1,4anhydroerythritol, derived from starch-based erythritol [36,37]. When 1,4-anhydroerythritol was hydrogenated by 1a under our reaction conditions, it afforded THF in modest yield (23%, entry 5).

The hydrogenolysis of epoxides catalyzed by **1a** and **1b**, proceeded smoothly under standard reaction conditions, generating various reduction products depending on the substrate.



Scheme 2. Ru-sulfoxide catalyzed hydrogenolysis of glycols and epoxides.

Thus, styrene oxide produced 2-phenethyl alcohol (34%), phenyl acetaldehyde (20%) and ethyl benzene (15%) (entry 6). Similarly, 1,2-hexene oxide was converted to 1-hexanol (40%) and hexanal (11%) (entry 7). On the other hand, cyclohexene oxide afforded cyclohexene (64%) and cyclohexanone (11%) (entry 8). In a separate experiment cyclohexene was found to be inert to hydrogenation catalyzed by **1a**.

The presence of carbonyl and mono-alcohol products in many of the glycol and epoxide reactions led us to consider them as possible reaction intermediates and hence to ascertain this we evaluated their hydrogenation in the present system. When the activated ketone, acetophenone, was subjected to our standard reaction conditions, ethyl benzene, from complete hydrogenolysis, was produced quantitatively (entry 9) in 24h, signifying the intermediacy of ketones in alkane formation. In contrast to this, its constitutional isomer, phenyl acetaldehyde, gave 2-phenyl ethanol in 72% yield (run 11), confirms the aldehyde as intermediate for mono-alcohol formation. The unactivated aldehvde hexanal is slowly converted to the corresponding alcohol, hexanol, in 19% yield while leaving 42% unreacted hexanal (entry 10). The similar observations were made in case of epoxides, where carbonyl compounds are being intermediates during hydrogenolysis process. Interestingly, aliphatic mono alcohols deoxygenated under the present reaction conditions to yield hydrocarbons (entries 12 and 13). In contrast, 2-phenethyl alcohol under the same reaction conditions was unchanged. This indicates that further reduction of phenethyl alcohol is unlikely under the present reaction conditions. Our observation of the hydrogenolysis reactions of glycols and epoxides catalyzed by **1a,b** have little precedent in homogeneous Ru-catalysis except for the glycol to alkane hydrogenation catalyzed by $[LRu(H_2O)_x(diimine)]^{2+}$ complexes [19-21]. In fact we can find no reports of complex 1a,b serving as a hydrogenolysis pre-catalyst for any class of substrates.

The catalytic pathways for hydrogenolysis promoted by 1a,b are presently unclear. However, the similar products formed from both diols and epoxides, suggests the participation of common organic intermediates i.e. carbonyl compounds (Scheme 3). Existing precedents [19-21.38-44] and our initial findings suggest that two cyclic pathways (I and II) are viable, as shown in Scheme 3. We suggest the hydrogenative loss of one chloride ligand to generate L₄RuHCl+HCl and the initial reaction proceeds through an ionic mechanism. Cycle I involves in formation of mono-alcohol from diol. In path A, acid catalyzed dehydration generates aldehyde; whereas in path **B**, epoxide rearranged to aldehyde. The C=O bond of the intermediate aldehyde would be hydrogenated via an ionic hydrogenation mechanism, which involve protonation of the aldehyde by L₄RuHCl·HCl followed by hydride transfer from L₄RuHCl to give mono-alcohol. Similar ionic hydrogenation of ketones promoted by Mo- and W are known [45-50]. Formation of alkene or alkane from diols (entries 2-6, 8, 9) can be explained as shown in cycle II (Scheme 3), involves in dehydration followed by reduction sequence. The mono-alcohol formed is further dehydrating to the alkene, which in turn get reduced to alkane (cycle II, Scheme 3). In another experiment, hydrogenation of 1-hexene produced hexane in 30% yield in 22 h under standard condition, which supports this hypothesis.

The hydrogenolysis of cyclohexene oxide mostly to cyclohexene may be the result of easier dehydration of the intermediate cyclohexanol (a trace amount of cyclohexanol was detected, entry 6). With respect to intervening Rucomplexes, the prevalence of alcohols promoted by **1a** may suggest the involvement of ionic intermediates, implicated in the Bullock–Fagan studies of glycol mono-hydrogenolysis [19–21].

Table 1

Ru-sulfoxide catalyzed hydrogenolysis of glycols and epoxides.

Entry	Substrate	Product(s)	Yield (%)	Time (h)
1	OH Ph OH	Ph	83 (78) ^d	8
2	ОН	\sim	58	8
3	"	"	62	3 ^b
4	OH H ₃ C OH	OH	9 Trace 36	96 ^c
5	но О-ОН	$\hat{\mathbf{O}}$	23	48
6	Ph	Ph OH Ph O Ph Ph	34 (35) ^d 20 (18) ^d 15 (17) ^d	30
7	~~~~ ⁰	{0H	40 18	8
8	o		64 11	8
9	Ph	Ph	99	24
10	~~~~\$ ⁰	∕∕∕⁄OH	19	24
11	Ph	Ph	72	52
12	ОН	\sim	43	24
13	OH		18	24

^a0.14 mmol glycol or epoxide in benzene (6–10 mL), 0.014 mmol *cis*-[Ru(TMSO/DMSO)₄], 190 °C, 6.8 atm H₂; yields determined by GC and GC–MS with n-dodecane as internal standard.

^b Reaction at 120 °C.

^c Reaction at 200 °C, 28 atm H₂.
^d Yields in parenthesis represents the reactions used *cis*-[Ru(DMSO)₄] catalyst.



Scheme 3. Plausible catalytic cycle for hydrogenolysis of glycols and epoxides.

3. Conclusion

In summary, we have developed a new reaction system for the selective deoxygenation of glycols and epoxides, to alcohols and/or alkanes, using H_2 as reductant and easily prepared *cis*-[RuCl₂(sulfoxide)₄] as catalyst. It is remarkable to note that the catalysts generate acid in situ; our system does not require any acid co-catalyst for dehydration. The product yields are moderate to excellent. Future investigations will focus on elucidating the important catalytic species and mechanisms of these reactions and their application to biomass-derived polyols.

4. Experimental

4.1. General details

Cis-[RuCl₂(TMSO)₄] [34] **1a** and *cis*-[RuCl₂(DMSO)₄] [35] **1b** were prepared by literature method. All other chemicals were purchased from Sigma–Aldrich and used as received. Hydrogenolysis reactions were performed in a 100 mL and 50 mL Parr steel autoclave (model 4792) fitted with glass liner.

5. General procedure for *cis*-[RuCl₂(TMSO)₄] or *cis*-[RuCl₂(DMSO)₄]-catalyzed hydrogenolysis of glycols and epoxides

In a Parr steel autoclave, **1a** or **1b** (0.014 mmol) and glycol/epoxide (0.14 mmol) and 5 μ L dodecane (internal standard) were added to anhydrous benzene (6–10 mL). The autoclave was pressurized to desired pressure (100, 400 psi) with molecular hydrogen and placed on a preheated oil bath to desired temperature (120°, 190°, 200 °C). The aliquots of samples were withdrawn at desired intervals and analyzed by GC and GC–MS.

Acknowledgements

Financial support from the Louisiana Board of Regents (RSS) and from the Oklahoma Bioenergy Center (KMN) is greatly appreciated.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j. molcata.2012.07.025.

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