RSC Advances

ROYAL SOCIETY OF CHEMISTRY

PAPER

View Article Online
View Journal | View Issue

Cite this: *RSC Adv.*, 2025, **15**, 21424

Transformation of PET-derived 1,4-benzenedimethanol to make useful alcohols†

Chandrika Ghosh, Raymundo Marcial-Hernandez, Matthew J. Andrews and Amit Kumar*

Received 22nd May 2025
Accepted 6th June 2025

DOI: 10.1039/d5ra03609g

rsc.li/rsc-advances

We report here a catalytic method to transform 1,4-benzenedimethanol to 3-(4-(hydroxymethyl)phenyl)propan-1-ol by coupling 1,4-benzenedimethanol with ethanol using a ruthenium catalyst. Through systematic optimization of catalytic conditions, a high TON of up to 400 000 has been achieved. Based on previous studies and those reported herein, we suggest that the reaction proceeds *via* a hydrogen-borrowing mechanism. Further conversion of 1,4-benzenedimethanol and 3-(4-(hydroxymethyl)phenyl)propan-1-ol through selective hydrodeoxygenation to make useful alcohols has also been demonstrated.

Introduction

The development of efficient and cost-effective processes for the chemical recycling of plastic waste such as PET (polyethylene terephthalate) is crucial for a circular economy. The area has received significant attention in the past couple of decades, and even large-scale processes for the chemical recycling of PET have been demonstrated or are in operation.[1,2] These processes are mainly based on methanolysis, glycolysis, and hydrolysis and produce ethylene glycol and terephthalic acid or corresponding esters that can be reused as feedstock to produce virgin PET. However, the cost of PET produced from chemical recycling can be higher than that produced directly from crude oil.[3,4] This challenge can potentially be tackled by developing methods to upcycle PET waste and make products of higher value than that of PET.

Along the direction of chemical recycling, the approach of catalytic hydrogenation has also been investigated for the depolymerization of PET waste.[5–9] The products obtained from this route are ethylene glycol and 1,4-benzenedimethanol. Although catalytic hydrogenation is a cleaner method for depolymerisation, and recent studies have developed efficient methods to depolymerise PET waste (*e.g.* 80 °C, 1 bar H_2, and turnover number (TON) up to 1520),[9] the demand for 1,4-benzenedimethanol is rather limited and significantly lower than the supply of PET waste. For the recycling of PET using hydrogenation to be viable, it is therefore important to develop new processes where 1,4-benzenedimethanol can be used as a feedstock to make useful products.

In particular, we were interested in making new alcohols due to their potential applications in making a range of organic compounds such as carboxylic acids, esters, and amides.[10] In this direction, Guerbet coupling using the hydrogen borrowing approach has attracted significant interest to upgrade alcohols, for example, to convert ethanol to butanol.[11–13] A range of homogeneous catalysts has been reported[11,14–21] for this transformation, some with very high TON such as 18 209.[22–25] We envisioned that this approach could be used to upgrade 1,4-benzenedimethanol that can be produced from the hydrogenative depolymerization of polyethylene terephthalate.[6,26] With this motivation, we report here our investigation on the transformation of 1,4-benzenedimethanol to make other useful alcohols.

Results and discussion

We started our investigation by studying the coupling of 1,4-benzenedimethanol (**1**) (2.5 mmol) with ethanol (**2**) (1 mmol) using transition-metal-based homogeneous catalysts known for the dehydrogenation of alcohols.[27–31] The aim was to optimise reaction conditions to form the maximum yield and selectivity for 3-(4-(hydroxymethyl)phenyl)propan-1-ol (**3**) or/and 1,4-benzenedipropanol (**4**) while obtaining a high TON (*e.g.* >1000) of catalyst at the same time. It is worth noting that the combination of catalyst and base needs to perform a number of transformations as per the hydrogen-borrowing mechanism – (a) dehydrogenate 1,4-benzenedimethanol and ethanol to form corresponding aldehydes, (b) perform cross-aldol condensation of both the aldehydes to form alkenes with the elimination of water, and (c) hydrogenate the formed alkene intermediates to make alkylated alcohols which are the desired products. The kinetics of the individual steps and the nature of catalysts/reaction conditions can play a huge role in achieving the desired selectivity as there are a number of side reactions that

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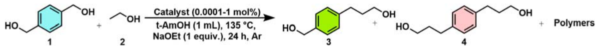
EaStCHEM, School of Chemistry, University of St Andrews, North Haugh, St Andrews, KY16 9ST, UK. E-mail: ak336@st-andrews.ac.uk

† Electronic supplementary information (ESI) available. See DOI: https://doi.org/10.1039/d5ra03609g

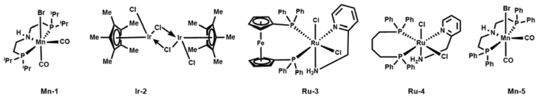
would need to be avoided such as (a) acceptorless dehydrogenative coupling of ethanol to form ethyl acetate, (b) Guerbet coupling of ethanol to form butanol, (c) acceptorless dehydrogenative polymerisation of 1,4-benzenedimethanol to form polyester, and (d) hydrogen borrowing polymerisation of 1,4-benzenedimethanol to form polyether or polyesterether. Additionally, the catalyst needs to remain tolerant to water that will be produced during the course of the reaction to achieve a high TON. Considering such demanding outputs, we performed a systematic study of catalytic conditions with the variation of precatalysts, base, solvent, temperature, and relative concentration of 1,4-benzenedimethanol and ethanol.

Initial reactions were conducted using 1 mol% precatalyst (**Mn-1**, **Ir-2**, **Ru-3**, **Ru-4**, **Mn-5**), NaOEt (1 mmol) at 135 °C for 24 h in a sealed 10 mL Young's flask in *t*-AmOH solvent. These reaction conditions were inspired by previous work conducted on the Guerbet coupling (ethanol to butanol) using such catalysts.[11,27] A higher concentration of 1,4-benzenedimethanol relative to ethanol was used to avoid self-coupling of ethanol to butanol. Interestingly, complex **Mn-1** led to the formation of 3-(4-(hydroxymethyl)phenyl)propan-1-ol (**3**) in 66% yield (relative to ethanol), and the formation of butanol was not observed by the GC-MS (Table 1, entry 1). The formation of 1,4-benzenedipropanol (**4**) was observed in only 1% yield. The remaining 1,4-benzenedimethanol was either unreacted or led to the formation of an oligomer containing alkyl and aromatic fragments of $M_n = 823$ Da (see ESI, Sections 2.4 and 6.4†). A similar result was obtained using the iridium complex **Ir-2** under identical conditions, which has also been reported for the coupling of benzyl alcohol with ethanol in the past (entry 2). Remarkably, ruthenium complexes **Ru-3** and **Ru-4** led to the formation of 3-(4-(hydroxymethyl)phenyl)propan-1-ol (**3**) in 91% and 86% yields, respectively (entries 3, 4). A lower yield (30%) was obtained in the case of manganese MACHO pincer complex **Mn-5** (entry 5). Considering the high performance of complexes **Ru-3** and **Ru-4**, we chose them for further optimization. Performing the catalysis using **Ru-3** but in the presence of different bases (NaOH and KO^{t}Bu) instead of NaOEt led to lower yields of 3-(4-(hydroxymethyl)phenyl)propan-1-ol (**3**) (entries 6 and 7). Based on these, we chose **Ru-3** and NaOEt to be the best catalytic combination. Performing the catalytic reaction using **Ru-3** and NaOEt in 1,4-dioxane instead of *t*-AmOH lowered the yield of 3-(4-(hydroxymethyl)phenyl)propan-1-ol (**3**) (entry 8), with toluene or THF performing similarly poorly (Table S1†). Interestingly, a higher yield (88%) was also obtained when the reaction was performed without using any solvent (entry 9).

Table 1 General procedure for the synthesis of 3-(4-(hydroxymethyl)phenyl)propan-1-ol (**3**) from 1,4-benzene dimethanol and ethanol *via* Ru(II)/Mn(I)/Ir(I)-catalyst[a]



Entry	Catalyst	Catalyst loading (mol%)	**3**^{b} (Yield %)	**4**^{b} (Yield %)	TON
1	**Mn-1**	1.0	66	1	66
2	**Ir-2**	1.0	69	5	69
3	**Ru-3**	1.0	**91**	**2**	**91**
4	**Ru-4**	1.0	**86**	**14**	**86**
5	**Mn-5**	1.0	30	0	30
6^c	**Ru-3**	1.0	32	0	32
7^d	**Ru-3**	1.0	69	0	69
8^e	**Ru-3**	1.0	41	1	41
9^f	**Ru-3**	1.0	88	0	88
10^g	**Ru-3**	1.0	70	0	70
11^h	**Ru-3**	1.0	15	0	15
12^i	**Ru-3**	**0.01**	**81**	**3**	**8100**
13^i	**Ru-4**	**0.01**	**75**	**1**	**7500**
14^i	**Ru-4**	**0.0001**	**37**	**0**	**370 000**
15^i	**Ru-3**	**0.0001**	**40**	**0**	**400 000**
16	**No catalyst**	**–**	**15**	**0**	**15**
17^j	**Ru-3**	1.0	0	0	0
18^k	**Ru-3**	1.0	48	32	48



[a] General reaction conditions: 1,4-benzenedimethanol (**1**) (2.5 mmol), NaOEt (1 mmol), metal-complex (1 mol%), ethanol (**2**) (1 mmol), and *t*-AmOH (1 mL) were placed in a 10 mL J-Young's ampule under an argon atmosphere and heated at 135 °C for 24 h; the mol% of the metal-complex depends on the amount of ethanol. [b] The yields are determined by ^{1}H NMR analysis using 1,3,5-trimethoxybenzene as an internal standard. [c] NaOH was taken as a base. [d] KO^{t}Bu was taken as a base. [e] 1,4-Dioxane was taken as a solvent. [f] No solvent was taken. [g] The reaction temperature was 150 °C. [h] The reaction temperature was 100 °C. [i] The reactions were scaled up by a factor of 20, and carried out in a 150 mL pressure vessel. [j] No base was used. [k] 1.5 mmol of 1,4-benzenedimethanol was taken.

Increasing or decreasing the temperature from 135 °C also lowered the yields (entries 10 and 11). Based on these experiments, our best catalytic conditions are complex **Ru-3** or **Ru-4**, NaOEt (1 equivalent relative to ethanol), 135 °C and 24 h.

Having established these, we wanted to see how far we could push the TON of precatalysts **Ru-3** and **Ru-4**. Remarkably, using 0.01 mol% catalytic loading of **Ru-3** led to the formation of 3-(4-(hydroxymethyl)phenyl)propan-1-ol (**3**) in 81% yield making the TON 8100 (entry 12). A similar TON (7500) was obtained when **Ru-4** was used keeping the remaining conditions the same (entry 13). Remarkably, we managed to push the TON further up and achieved 40% and 37% yields using 0.0001 mol% loading of complexes **Ru-3** and **Ru-4** making the TON 0.4 million and 0.37 million, respectively (entries 14 and 15). These experiments however required the addition of *t*-AmOH for efficient mixing. Performing the reaction without using any transition–metal complex but in the presence of NaOEt also led to the formation of 3-(4-(hydroxymethyl)phenyl)propan-1-ol (**3**) in 15% yield, suggesting that some background transformation can occur just in the presence of the base (entry 16). Performing the reaction just in the presence of complex **Ru-3** without using any base did not lead to any conversion of the starting material, suggesting the crucial role of base in the catalyst activation phase as well as other catalytic stages (entry 17).

Based on previous studies,[23] the process likely undergoes through hydrogen-borrowing mechanism. This mechanism was probed through the use of *trans*-chalcone. In the presence of either 1,4-benzenedimethanol (**1**) or ethanol (**2**) under standard reaction conditions, hydrogenated products were observed, supporting *in situ* H_2 generation from these components (Fig. 1A). Such products were not observed in the absence of **1** or **2**. Other control experiments of coupling **2** showed mainly the formation of butanol, with other higher aromatics, as previously reported in literature[27] (Fig. 1B), whilst coupling of benzyl alcohol, as a substitute for **1**, showed traces of esters and aldehyde, supporting the dehydrogenation of **1** (see ESI, Section 4†). The hydrogen-borrowing mechanism is further supported by GC-TCD analysis of the headspace. In the control reactions (Fig. 1A), and as per Table 1, entry 3, H_2 gas was observed. No other gases *e.g.* CO or CO_2 were detected. Although in an ideal hydrogen-borrowing no H_2 should be evolved, we suspect the formation of H_2 is likely due to the dehydrogenation of remaining 1,4-benzenedimethanol as it is used in excess under the reaction conditions.

On this basis we suggest that the process undergoes a hydrogen-borrowing transformation as outlined in Fig. 2A. The first step is likely to be the dehydrogenation of 1,4-benzenedimethanol and ethanol to form 4-(hydroxymethyl)benzaldehyde and acetaldehyde, respectively. This is followed by cross-aldol condensation between both the aldehydes to form an alkene intermediate that can subsequently be hydrogenated to form 3-(4-(hydroxymethyl)phenyl)propan-1-ol (**3**). In addition to the formation of **3** and **4** (Table 1), we also observed the formation of a white precipitate in <20% yield (by weight) which were characterized to be a mixture of higher diols and polymers containing alkyl, aryl, and ester linkages of M_n in the range of 365–17675 Da (see ESI, Sections 2.4 and 6.4†). Indeed, performing the reaction of 3-(4-(hydroxymethyl)phenyl)propan-1-ol (**3**) with ethanol under similar reaction conditions led to the formation of 1,4-benzenedipropanol (**4**) in 60% yield, suggesting the possibility of the formation of higher alcohols (Fig. 2B). Preference for **4** is observed, opposed to the formation of longer chained alcohol, or homo-condensation. This is postulated to be due to conjugation between the hydroxybenzyl group with the aromatic ring. The formation of ester is possible *via* the dehydrogenation of hemiacetal intermediate as outlined in Fig. 2C.

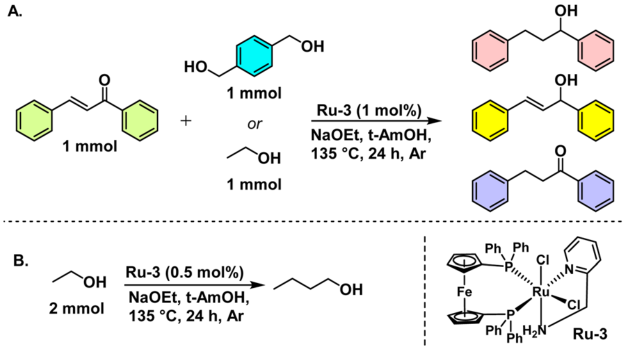


Fig. 1 Mechanistic investigation though (A) hydrogenation of *trans*-chalcone under reaction conditions, and (B) Guerbet coupling of ethanol to form butanol.

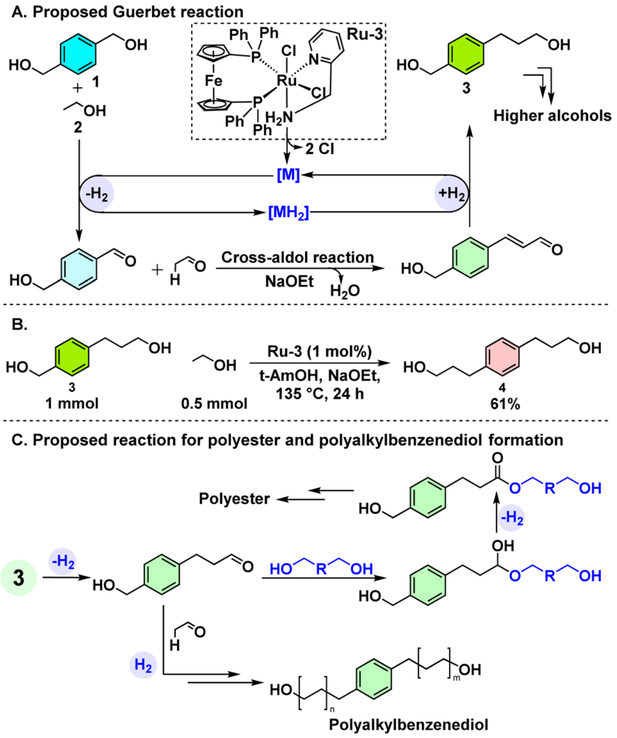


Fig. 2 (A) Proposed pathway for the Guerbet coupling of 1,4-benzenedimethanol with ethanol to form higher diols **3**. (B) Synthesis of **4** from **3** with ethanol using Ru-3 complex *via* Guerbet coupling. (C) Proposed pathway for the coupling of 1,4-benzenedimethanol with ethanol to form polymers.

Having studied the coupling of 1,4-benzenedimethanol with ethanol, we investigated the selective hydrodeoxygenation of 1,4-benzenedimethanol (**1**) and 3-(4-(hydroxymethyl)phenyl)propan-1-ol (**3**). Inspired by the work on the hydrodeoxygenation of aromatic alcohols using heterogeneous catalysts,[32] we studied the hydrodeoxygenation of 1,4-benzenedimethanol using Ru/Al_2O_3. However, using 50–80 bar H_2 at 150 °C, 24 h in *t*-AmOH, ethanol, or a combination of ethanol and 2-MeTHF led to the hydrogenation of the aromatic ring and the formation of 1,4-cyclohexanedimethanol with the *cis* isomer as a major product (*e.g.* *cis*/*trans* ratio of 2.4 : 1, Fig. 3A). Interestingly, we observed the formation of the *trans* isomer as a major product when the reaction was conducted under neat conditions (without using any solvent, *cis*/*trans* ratio of 1 : 3.3). It is noteworthy that 1,4-cyclohexanedimethanol is used to make commercial polyesters and the isomer composition of the monomers can affect the polymer properties.

We also studied hydrodeoxygenation using PMHS (polymethylhydrosiloxane) as a reducing agent as it has been considered a green and sustainable reducing agent.[33] Inspired by a previous report on hydrodeoxygenation of benzylic alcohols,[34] we studied this reaction using $PdCl_2$ as a catalyst. Interestingly, the reaction of 1,4-benzenedimethanol using 3 equivalents of PMHS in the presence of 5 mol% $PdCl_2$ in ethanol at room temperature (4 h) led to the formation of *p*-xylene and 4-methyl benzyl alcohol in 80%, and 18% yields, respectively (Fig. 3B). Performing the hydrodeoxygenation of 3-(4-(hydroxymethyl)phenyl)propan-1-ol (**3**) under this condition did not lead to any conversion of the starting material. However, when the reaction temperature was raised to 50 °C, 3-(*p*-tolyl)propan-1-ol (**7**) and 1-methyl-4-propylbenzene (**8**) were obtained in 78% and 1% yields, respectively (Fig. 3C). It is noteworthy that alcohols **3** and **7** have been considered as feedstock to make pharmaceutically relevant molecules.[35–37]

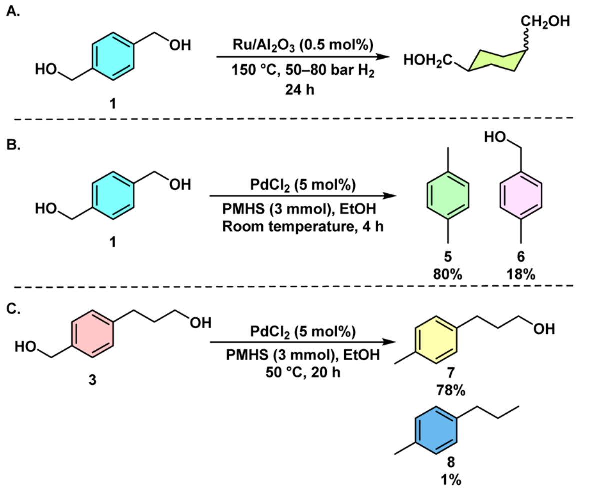


Fig. 3 (A) Synthesis of 1,4-cyclohexanedimethanol (*cis*/*trans* mixture) from 1,4-benzenedimethanol using Ru/Al_2O_3 catalyst. (B) Hydrodeoxygenation of 1,4-benzenedimethanol using $PdCl_2$ and polymethylhydrosiloxane (PMHS). (C) Hydrodeoxygenation of 3-(4-(hydroxymethyl) phenyl) propan-1-ol (**3**) using $PdCl_2$ and polymethylhydrosiloxane (PMHS).

Conclusions

In conclusion, we report here a highly active catalyst for the coupling of 1,4-benzenedimethanol with ethanol to form 3-(4-(hydroxymethyl)phenyl)propan-1-ol. A TON up to 0.4 million has been achieved using a ruthenium complex **Ru-3**. Based on our mechanistic studies and previous report, we suggest that the transformation occurs *via* a hydrogen-borrowing pathway, as described in Fig. 2. Additionally, we also report our studies on the hydrogenation and hydrodeoxygenation of 1,4-benzenedimethanol to make 1,4-cyclohexanedimethanol and *p*-xylene. 3-(4-(Hydroxymethyl)phenyl)propan-1-ol (**3**) was selectively hydrodeoxygenated to make 3-(*p*-tolyl)propan-1-ol (**4**).

Data availability

The raw research data supporting this publication can be accessed at https://doi.org/10.17630/bfd4eb7a-f98b-406b-85ae-41f53f5485e5. The data supporting this article have been included as part of the ESI.†

Author contributions

A. K. and C. G. conceived the concept. C. G. performed the experiments and prepared the ESI.† R. M. H. and M. J. A. contributed to the analysis of products from catalytic reactions. A. K. supervised the project and prepared the manuscript with contributions from others. All authors have given approval to the final version of the manuscript.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This research is funded by EPSRC (selected by ERC, EP/Y005449/1). The authors thank the School of Chemistry, University of St Andrews, Central Instrumentation Facility for the use of NMR and HRMS facilities.

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