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Direct Synthesis of Cycloalkanes from Diols and Secondary Alcohols or Ketones Using a Homogeneous Manganese Catalyst

Akash Kaithal,†,‡ Lisa-Lou Gracia,‡ Clément Camp,‡ Elsje Alessandra Quadrelli,‡ and Walter Leitner†,§

†Institut für Technische und Makromolekulare Chemie, RWTH Aachen University, Worringer Weg 2, 52074 Aachen, Germany
‡Laboratory of Chemistry, Catalysis, Polymers and Processes, C2P2 UMR 5265, Université de Lyon, Institut de Chimie de Lyon, CNRS, Université Lyon 1, ESCPE Lyon, 43 Bd du 11 Novembre 1918, F-69616 Villeurbanne, France
§Max Planck Institute for Chemical Energy Conversion, Stiftstraße 34-36, 45470 Mülheim a.d. Ruhr, Germany

Supporting Information

Abstract: A method for the synthesis of substituted cycloalkanes was developed using diols and secondary alcohols or ketones via a cascade hydrogen borrowing sequence. A non-noble and air-stable manganese catalyst (2 mol %) was used to perform this transformation. Various substituted 1,5-pentanediols (3–4 equiv) and substituted secondary alcohols (1 equiv) were investigated to prepare a collection of substituted cyclohexanes in a diastereoselective fashion. Similarly, cyclopentane, cyclohexane, and cycloheptane were constructed from substituted 1,4-butanediol, 1,5-pentanediol, and 1,6-hexanediol, and sterically hindered ketones following a (4 + 1), (5 + 1), and (6 + 1) strategy, respectively. This reaction provides an atom economic methodology to construct two C–C bonds at a single carbon center generating high-value cycloalkanes from readily available alcohols as feedstock using an earth-abundant metal catalyst.

Cycloalkanes are ubiquitous structural motifs in natural products, pharmaceuticals, or materials. In the past, substantial efforts have been devoted to the development of synthetic strategies to build cycloalkane scaffolds. Among the methods to synthesize substituted cyclohexanes one can mention Diels–Alder cycloadition (4 + 2) followed by reduction, hydrogenation of aromatic six-membered rings, cyclization of dihalides via Wurtz reaction, dimerization of cyclopropanes, and Michael reaction on enolizable reagents. All these approaches have some drawbacks such as multistep procedures, poor regio- or stereoselectivity, narrow substrate scope, or the generation of a stoichiometric amount of chemical waste. The preparation of substituted cycloheptane rings is an even bigger challenge. At present, very few organic syntheses are known to accomplish the formation of seven-membered rings from noncyclic common chemicals. Simple cycloheptane derivatives are typically produced via the reduction of cycloheptanone or cycloheptenes. Multistep procedures for the preparation of substituted cycloheptane-1,3-diones, which on reduction can produce substituted cycloheptane rings, were reported from 1,2-diketones and ring expansion of cyclopentanones. As a catalytic method, ring closing metathesis (RCM) followed by hydrogenation has generated a significant impact addressing the challenge to synthesize medium size aliphatic rings. Cycloisomerization followed by hydrogenation can also be considered as a possible synthetic route. However, these strategies require the dedicated synthesis of very specific starting materials containing the functional groups in perfect arrangement to allow for the cyclization step. Developing a straightforward, sustainable and one-step process to construct the high-value cycloalkane rings from simple building blocks is therefore an important challenge for catalysis to open new retrosynthetic pathways to these important structural units.

We report herein a broadly applicable synthetic route to cyclopentanes, cyclohexanes, and cycloheptanes from α−ω diols (n-C6, n-C7, and n-C8, respectively) via coupling with secondary alcohols or ketones. Alcohols and diols are ubiquitous starting materials including biomass-derived substrates making them very attractive as cheap sources for the preparation of essential and challenging building blocks. Especially C–C bond forming reactions via hydrogen-borrowing methodologies have gained significant attention recently. For example, metal-catalyzed β-alkylation of alcohols and α-alkylation of ketones following this principle are well-established (Scheme 1-A). Recently, we reported the ruthenium and manganese catalyzed selective β-methylation of alcohols using methanol as a C1 source (Scheme 1-B). Based on this experience, we speculated whether a similar approach could also be applicable for the preparation of cycloalkane rings using diols via a double alkylation methodology. Akhtar and co-workers reported the synthesis of substituted cyclohexanes using sterically hindered 1-(2,3,4,5,6-pentamethylphenyl)ethanone and diols applying a noble-metal iridium catalyst. However, the reaction was exclusively restricted to the specific bulky ketone. Gratifyingly, we found that complex [Mn(CO)2(Br)[HN(C2H5PPr2)2]], 1, known as Mn-MACHO-Pr, acts as a versatile catalyst for the desired reaction and makes this strategy a potentially very useful approach for the synthesis of cycloalkanes (Scheme 1-C). Initially, using 1 (2 mol %) in the reaction of a stoichiometric mixture of 1-phenylethanol 2a and 1,5-
pentanediol 3a in the presence of KO'Bu (4 equiv) as a base gave only 16% yield of 4a. The low yield can be attributed to the self-condensation of the diol as a side reaction, as corroborated by the observation of the corresponding lactone by GC-MS analysis. Increasing the diol-to-alcohol ratio of 2:1 improved the yield of 4a to 47%, along with unreacted starting material and acetoephone (Table 1, entry 2). Interestingly, the Mn-catalyst 1 gave a higher yield when compared to the closely related ruthenium(II) catalyst Ru-MACHO-BH that leads to 35% of 4a under the same conditions. This example highlights further the opportunities to use Mn(II) as a proxy for Ru(II) in pincer frameworks due to the diagonal relationship in the periodic table. Varying the diol amount further led to a maximum of yield and selectivity of 62% 4a at 82% conversion at a 4:1 ratio (Table 1, entries 3–5). Only minor amounts of side products stemming from aldol-type reactions of 1-phenylethanol were observed under these optimized conditions (see the SI for details).

Reducing the temperature to 120 °C gave very low conversion (Table 1, entry 6). Increasing the temperature to 170 °C gave higher conversion of 98% and yield of 74% (Table 1, entry 7) while the selectivity remained virtually constant as compared to 150 °C. Decreasing the catalyst loading from 2 mol % to 1 mol % diminished the product yield and showed only 36% product formation at 86% conversion (Table 1, entry 8). Altering the base from KO'Bu to Cs2CO3 and NaO'Bu also led to low product formation (Table 1, entries 9 and 10). Finally, prolonging the reaction time from 24 to 32 h at 2 mol % catalyst loading with KO'Bu resulted in the best catalytic performances with 80% GC yield and 72% isolated yield after purification by column chromatography (Table 1, entry 11). Under these optimized conditions, diol 3a could be replaced with 3-methylpentan-1,5-diol 3b leading to even higher yields of 4b (92% yield by GC and 81% isolated yield, Table 1, entry 12). The trans-products with both sterically demanding groups in the equatorial positions are typically the thermodynamically favored isomers. This arrangement was confirmed by NMR analysis and DFT calculations with a diastereomeric ratio of 90:10 in favor of the trans-isomer for 4b in the isolated product (see SI for the assignment of the stereochemistry).

Based on these optimized reaction conditions, several secondary alcohols with different functional groups and varying steric demands were reacted with 3-methylpentan-1,5-diol 3b in order to explore the scope of the reaction (see Chart 1). Replacing the phenyl ring with a naphthyl ring afforded the corresponding product 4c in 86% GC yield and 83% isolated yield with a 87:13 diastereomeric ratio. Methyl substitution of 1-phenylethanol in the para- or ortho-position also gave the cyclohexyl product in high yield with the preferential formation of the trans-diastereomer (Chart 1, 4d and 4e). Reaction with the para-methoxy substituted secondary alcohol afforded the desired product in high yield (78% GC yield), while the ortho-methoxy substituted derivative showed somewhat lower selectivity (52% GC yield, see Chart 1, 4f and 4g). The reaction with 1-(4-chlorophenyl)ethanol showed excellent conversion but resulted in the formation of a mixture of products under standard conditions. However, when the reaction time was decreased to 14 h, the desired cyclohexyl product 4h was obtained in up to 70% GC yield and 61% isolated yield with very high selectivity to trans-diastereomer (Chart 1, entry 4h). Bromo substitution in the para-position of 1-phenylethanol showed a 40% yield to the corresponding cyclohexyl product 4i after 14 h reaction time. However, debromination also occurred accounting for another 33% of cyclization product. Interestingly, heterocyclic-secondary alcohol 1-(furan-2-yl)ethan-1-ol also revealed 61% isolated yield to the cyclohexyl product 4j.

Aliphatic alcohols comprising less acidic β-CH proton than the benzylic substrates also reacted smoothly. 1-Cyclohexylethanol yielded the desired cyclohexyl product 4k in good yield. However, in this case, low diastereomeric selectivity was observed (Chart 1, entry 4k). Small aliphatic secondary alcohols such as 3-methylbutan-2-ol and isopropyl...
alcohol also confirmed good reactivity and high selectivity to the trans-diastereomer (Chart 1, entry 4l, 4m). By using isopropyl alcohol as a substrate two cyclohexyl ring formations were made possible.

Next, a variety of alkyl and aryl substituted diols were coupled with a range of secondary alcohols using the same optimized reaction conditions. The corresponding cyclohexane products were obtained in very good yields and with fair to high diastereoselectivity, further confirming the general efficiency and versatility of this synthetic methodology (Chart 1).

Assuming that dehydrogenation of the secondary alcohol is a crucial step in the reaction sequence (vide infra), ketones 5a and 5b were also tested in the reaction (see Chart 2).

| Conversion (%) / GC Yield (Isolated Yield) |
|------------------------------------------|
| ![Chart 1](chart1.png)                     |

| Conversion (%) / GC Yield (Isolated Yield) |
|------------------------------------------|
| ![Chart 2](chart2.png)                     |

"Reaction conditions: secondary alcohol 2 (0.5 mmol), diol 3 (2 mmol), Mn-complex 1 (5 mg, 2 mol %), KO'Bu (224 mg, 2 mmol), and toluene (2 mL) were heated in a closed vessel. Conversion and yield were calculated using GC analysis. Yields in parentheses correspond to isolated yields after purification via column chromatography. Reaction time: 14 h. 1.5 mmol of diol was used. Three mmol of diol and 4 mmol of KO'Bu were used. n.d.: not determined.

Interestingly, their use yielded selectively the ketone products; the corresponding alcohol derivatives were not observed. While the steric hindrance in these substrates reduced the reactivity to form the six-membered cycle somewhat giving only 52% yield of product 7d, it proved beneficial for synthesis of five- and seven-membered cycloalkanes. The reaction of 1,6-hexanediol with pentamethyl acetophenone 5a led to formation of the desired seven-membered ring species 7a with very good yield and high selectivity (78% GC yield and 66% isolated yield). Reaction of methyl substituted 1,6-hexanediol with 5a also provided to the cycloheptane product 7b with excellent 98% yield. The methyl substitution of the ketone derivative was reduced from 5a to 1-mesitylethanone 5b without altering the efficiency of the reaction (see formation of 7c in good yield: 78% by GC, 62% as isolated yield). The reaction of 5a with 1,4-butanediol gave the five-membered ring product in 46% yield (Chart 2). In a similar manner, the reaction of 5b with 1,4-butanediol afforded the expected cyclopentane derivative with a 39% yield. The reaction of secondary alcohols with 1,4-butanediol and 1,6-hexanediol to prepare five- and seven-membered rings revealed only a mixture of products. Similarly, attempts to prepare four-membered rings from 1,3-propanediol either with the ketone
or secondary alcohol did not yet yield synthetically useful yields.

The overall reaction of the new synthetic protocol requires a complex sequence of several individual transformations to assemble the cycloalkane rings. Several control experiments support the assumption that it follows a Guerbet-type de/rehydrogenation-condensation mechanism. Reactions without either complex I or KO'Bu did not show any product formation which confirmed that the reaction requires both the manganese complex and the base to achieve the desired reaction sequence. While the reaction with 1-phenyethanol 2a resulted in alcohol 4a as product (Table 1, entry 11), the coupling of sterically more hindered 1-mesitylethanol 8 with 1,5-pentanediol 3a resulted in the selective formation of ketone 9 as product with 37% isolated yield (Scheme 2). This can be rationalized assuming that ketone 5b is formed from 8 as intermediate, but the C=O group in the product cannot be rehydrogenated due to steric hindrance. To verify the hypothesis, the reaction of acetophenone 10 with 3b was performed. Indeed, the alcohol product 4b was obtained in 90% GC yield with a 86:14 diastereomeric ratio (Scheme 2), very similar to that obtained when starting from the alcohol 2a (Table 1, entry 12). Reacting deuterium-labeled 1-phenylethanol (1 equiv) 2a with 3b (4 equiv) gave product 4b with only very low deuterium content, confirming large degrees of H/D scrambling in agreement with a hydrogen borrowing mechanism (Scheme 2).

On the basis of these experimental data and literature precedence, a plausible reaction sequence illustrating the role of the Mn-catalyst and the base is proposed in Scheme 3 (a more detailed representation is given in the SI). In the presence of KO'Bu, complex I is converted to the amido complex I', a type of Mn(I) complexes that is well-known for its activity in hydrogen-transfer reactions. The formation was also verified by 31P NMR in the present case (see the SI). Deprotonation occurs via reaction of I with secondary alcohol A or dial B to Mn-alkoxy amino complexes II and II' followed by β-hydride elimination to give ketone B and aldehyde B', respectively. In the presence of base, aldol-condensation takes place between B and B' to form the corresponding enone C. The manganese hydride intermediate III that originates from β-hydride elimination rehydrogenates the C=O unit of C to the corresponding enol product D, thereby regenerating the active Mn-species I. Base-catalyzed allyl isomerization of enol D leads to the corresponding hydroxy ketone E, from which the analogous sequence starts again whereby intramolecular aldol-condensation fabricates the cyclic structure. Depending on the steric hindrance of the ketone moiety, the reaction may stop at product F or involve another rehydrogenation step to result in alcohol G as the final product.

In conclusion, we have developed an efficient and versatile synthetic strategy to prepare substituted cycloalkanes via catalytic coupling of diols and secondary alcohols/ketones using an earth-abundant and air-stable manganese pincer complex. Various aromatic and aliphatic secondary alcohols were coupled with several substituted 1,5-pentanediols to generate substituted cyclohexane rings with very good to high yield and moderate to high diastereoselectivity. Notably, the same methodology allows the catalytic synthesis of cycloheptane and cyclopentane rings by variation of the carbon chain in the diol component, reaching high to excellent yields for challenging cycloheptane derivatives. The reaction principle is atom economic producing only water as stoichiometric byproduct. Presently, however, an excess diol is required due to formation of intramolecular side products such as lactones. Further optimization to suppress this path would be facilitated by a more detailed understanding of the complex reaction network and the factors controlling the rates of the individual steps. While the Mn-catalyst affects primarily the de- and rehydrogenations steps, the base mediates probably the C–C bond formation and isomerization. Given the significant
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