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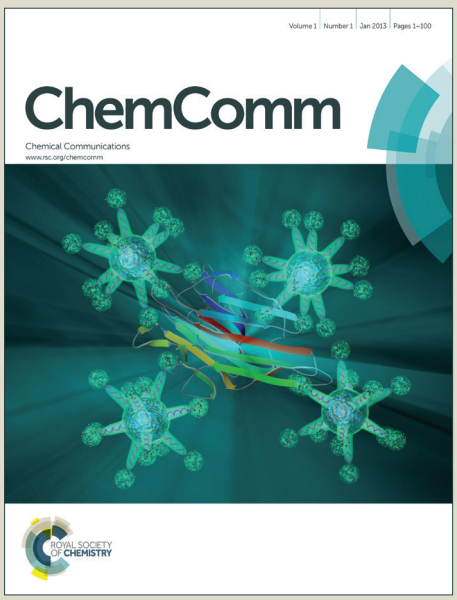

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Ruthenium pincer-catalyzed synthesis of substituted γ-butyrolactones using hydrogen autotransfer methodology

Cite this: DOI: 10.1039/x0xx00000x

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Received ooth January 2014,
Accepted ooth January 2014

DOI: 10.1039/x0xx00000x

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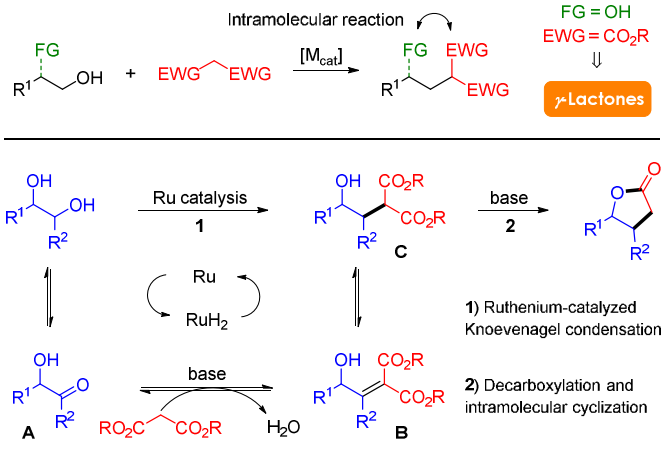
The ruthenium pincer-catalyzed synthesis of γ-butyrolactones from 1,2-diols and malonates using borrowing-hydrogen methodology is reported. This regioselective domino-process takes place through catalytic C-C bond formation, followed by intramolecular transesterification. Here, we show the Ru-MACHO-BH complex as a valuable catalyst on hydrogen autotransfer reactions.

γ-Butyrolactones are a common structural moiety present in a variety of natural products. They are usually taking part of more complex frameworks, especifically polycyclic ring systems, which display broad biological activities including antitumor, antiviral, antibiotic or antifungal properties among many others.[1] This relevance makes this unit very attractive for the discovery of novel potential drugs. Hence, the development of new synthetic methodologies for this class of compounds is of special interest. Altough a number of classical procedures for the synthesis of γ-butyrolactones are known, most of them require either specific substrates and/or rigorous reaction conditions.[2] For this reason, during the last years several research groups were interested to discover more efficient metal-catalyzed processes.[3] In addition, also metal-free strategies have been published for this purpose. For example, the groups of Glorius[4] and Bode[5] have succesfully used *N*-heterocyclic carbene (NHC) catalyzing conjugate umpolung of α,β-unsaturated aldehydes to synthesize different γ-butyrolactones. Alternatively, this methodology was also extended to other coupling partners as well as different carbene catalysts.[6]

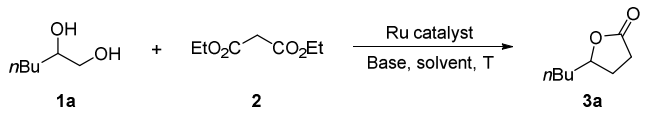
During the last decade, our research group showed a continuing interest in the so-called borrowing-hydrogen methodology, also known as hydrogen autotransfer process.[7] This procedure allows the activation of simple and available alcohols through a temporary metal-catalyzed oxidation to the corresponding aldehyde or ketone. Following condensation with amines and final reduction with the previously removed hydrogen, lead to amination of alcohols in an atom economy process as H_2O is generated as the only by-product.[8] Additionally, the synthesis of *N*-heterocycles by sequential dehydrogenative coupling processes has also been developed, where C-N and C-C bonds are simultaneously formed.[9] Notably, this methodology was also elegantly developed in the research groups of Williams and Yus for the C-C bond formation between C-nucleophiles and alcohols.[10] In this latter case, the Wittig or Knoevenagel reaction, as well as the aldolic condensation with the intermediate carbonylic compound, provided the corresponding C-alkylated products in a economical and environmentally benign way.

Inspired by the metal-catalyzed Knoevenagel condensation with alcohols, we propose that the introduction of a second appropriate functional group in the substrate might lead, after the C-C bond formation, to an intramolecular cyclization providing an heterocyclic compound (Scheme 1). Taken this premise into account, we planned to use 1,2-diols and malonates as reagents, which would allow to obtain the correponding lactones. In agreement with the established borrowing-hydrogen process for the formation of carbon-carbon bonds, the synthesis of γ-butyrolactones should proceed by the following domino sequence: temporary removal of hydrogen from the diol provides the corresponding 1,2-hydroxyketone **A**, which undergoes a Knoevenagel reaction with the malonate giving, after returning of the hydrogen initially extracted, the intermediate compound **C**. Finally, decarboxylative reaction followed by subsequent lactonization in basic medium affords the desired heterocyclic compound. Promisingly, this reaction cascade would allow us to generate sequentially for the first time a C-C and a C-O bond using this hydrogen autotransfer methodology. Under these assumptions, we present herein the first study into the ruthenium-catalyzed synthesis of substituted γ-butyrolactones by using 1,2-diols and malonates as substrates.



Scheme 1. Synthesis of γ-butyrolactones via ruthenium-catalyzed carbon-carbon bond formation between 1,2-diols and malonates.

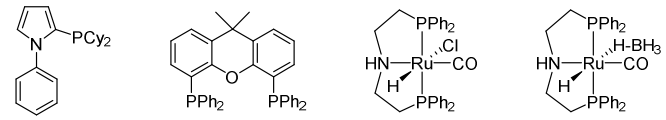
Table 1. Optimization of the reaction conditions for the synthesis of 5-butyldihydrofuran-2(*3H*)-one (**3a**) from 1,2-hexanediol (**1a**) and diethyl malonate (**2**).[a]



1a **2** **3a**

Entry	Catalyst	Base	Solvent	Yield (%)[b]
1	Ru_3CO_{12}	*t*BuOK	*t*-amyl alcohol	—
2	Ru_3CO_{12}/CataCXiumPCy	*t*BuOK	*t*-amyl alcohol	9
3	Ru_3CO_{12}/Xantphos	*t*BuOK	*t*-amyl alcohol	—
4	$[RuCl_2(p\text{-cymene})]_2$	*t*BuOK	*t*-amyl alcohol	11
5	$RuHCl(CO)(PPh_3)_3$	*t*BuOK	*t*-amyl alcohol	15
6	Ru-MACHO	*t*BuOK	*t*-amyl alcohol	27
7	Ru-MACHO-BH	*t*BuOK	*t*-amyl alcohol	32
8	Ru-MACHO-BH	NaOH	*t*-amyl alcohol	29
9	Ru-MACHO-BH	NaHMDS	*t*-amyl alcohol	28
10	Ru-MACHO-BH	K_2CO_3	*t*-amyl alcohol	36
11	Ru-MACHO-BH	Cs_2CO_3	*t*-amyl alcohol	26
12[c]	**Ru-MACHO-BH**	**K_2CO_3**	***t*-amyl alcohol**	**61**
13[d]	Ru-MACHO-BH	K_2CO_3	*t*-amyl alcohol	58
14[c,e]	Ru-MACHO-BH	K_2CO_3	*t*-amyl alcohol	53
15[c]	Ru-MACHO-BH	K_2CO_3	toluene	57
16[c]	Ru-MACHO-BH	K_2CO_3	1,4-dioxane	53
17[c,f]	Ru-MACHO-BH	K_2CO_3	*t*-amyl alcohol	42
18[c,g]	Ru-MACHO-BH	K_2CO_3	*t*-amyl alcohol	48
19[c,h]	Ru-MACHO-BH	K_2CO_3	*t*-amyl alcohol	45
20[c,i]	Ru-MACHO-BH	K_2CO_3	*t*-amyl alcohol	60
21[c]	Ru-MACHO-BH	—	*t*-amyl alcohol	7
22[c]	—	K_2CO_3	*t*-amyl alcohol	—

[a] Unless otherwise specified, all reactions were carried out with diol (**1a**, 1 mmol), malonate (**2**, 1.1 mmol), catalyst (0.02 mmol) and base (0.1 mmol) in a solvent (1 mL) at 150 °C for 18 h. [b] GC yields of the crude reaction mixture with hexadecane as internal standard. [c] Malonate (2 mmol). [d] Malonate (3 mmol). [e] Base (0.2 mmol). [f] Catalyst (0.01 mmol). [g] Catalyst (0.04 mmol). [h] Reaction temperature: 160 °C. [i] Reaction time: 24 h.

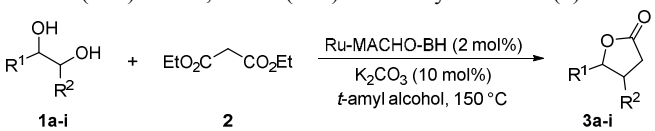


CataCXiumPCy Xantphos Ru-MACHO Ru-MACHO-BH

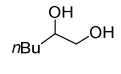
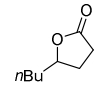
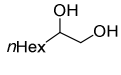
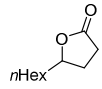
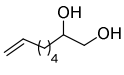
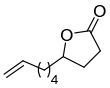
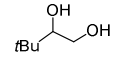
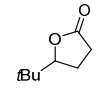
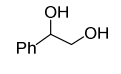
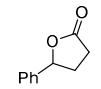
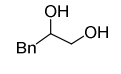
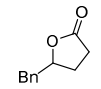
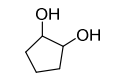
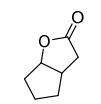
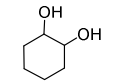
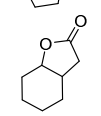
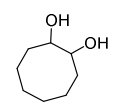
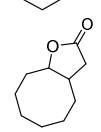
Our research started by selecting an effective ruthenium-based catalytic system for the model transformation between 1,2-hexanediol (**1a**, 1 mmol) and diethyl malonate (**2**, 1.1 mmol) in basic medium. Based on our previous experience,[8] we studied the reaction in the presence of $Ru_3(CO)_{12}$ (0.02 mmol) and *t*BuOK (0.1 mmol) as base in *t*-amyl alcohol at 150 °C. Initially, we observed no reaction under ligand free conditions, while the use of phosphines as ligands, well-known as metal reactivity moderators, did not improve too much the efficiency of the catalyst (9% yield observed with CataCXiumPCy as ligand, Table 1, entries 1-3). Other ruthenium sources also provided the corresponding lactone **3a** in low yields (11-15%, Table 1, entries 4 and 5), but complexes bearing aliphatic non-inocent PNP pincer ligands allowed to increase considerably the yield to 27 and 32% respectively (Table 1, entries 6 and 7). Recently, our group proved the utility of Ru-MACHO derivatives in a variety of (de)hydrogenation reactions.[11] Hence, we decided to explore different reaction conditions by using the commercially available Ru-MACHO-BH complex as catalyst. The study of several bases showed us that K_2CO_3 provided the best result (36%, Table 1, entries 8-11), while, fortunately, the reaction with 2 equivalents of diethyl malonate led to 5-butyldihydrofuran-2(*3H*)-one (**3a**) as the only regioisomer in a substantially higher 61% yield (Table 1, entry 12). Adding another equivalent of **2** did not promote a more effective reaction (Table 1, entry 13). Using higher amounts of base, other solvents and catalyst loadings, as well as higher reaction temperatures and times, resulted in even lower yields (Table 1, entries 14-20). Finally, the reaction without base only gave traces of the desired product, whereas the experiment in absence of catalyst showed no conversion (Table 1, entries 21 and 22). Thus, after this exhaustive screening we selected the reaction of 1,2-diol (1 mmol) and malonate (2 mmol) with Ru-MACHO-BH (0.02 mmol), K_2CO_3 (0.1 mmol) in *t*-amyl alcohol at 150 °C for 18 h as the optimal catalytic system. It is important to note that the reaction proceed regioselectively to give exclusively the 5-substituted γ-butyrolactone. Considering the overall reaction sequence, which involves at least six different intra- and intermolecular reactions (dehydrogenation, addition, H_2O elimination, hydrogenation, lactonization, decarboxylation), the optimized yield suggests that each individual step proceeds with very high efficiency.

Once chosen the best reaction conditions, we examined the scope and limitations of the optimized catalytic system. As shown in Table 2, different vicinal diols were effectively converted into the

Table 2. Ruthenium-catalyzed synthesis of substituted γ-butyrolactones (**3a-i**) from 1,2-diols (**1a-i**) and diethyl malonate (**2**).[a]



1a-i **2** **3a-i**

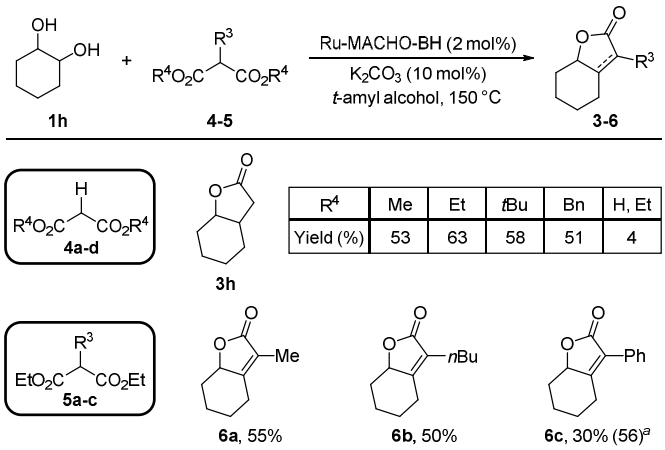
Entry	Diol		γ-Butyrolactone		Yield (%)[b]
1		(**1a**)		(**3a**)	61
2		(**1b**)		(**3b**)	52
3		(**1c**)		(**3c**)	56[c]
4		(**1d**)		(**3d**)	54
5		(**1e**)		(**3e**)	22
6		(**1f**)		(**3f**)	57
7		(**1g**)		(**3g**)	52
8		(**1h**)		(**3h**)	63
9		(**1i**)		(**3i**)	54

[a] Unless otherwise specified, all reactions were carried out with diol (**1a-i**, 1 mmol), malonate (**2**, 2 mmol), Ru-MACHO-BH (0.02 mmol) and K_2CO_3 (0.1 mmol) in *t*-amyl alcohol (1 mL) at 150 °C for 18 h. [b] Isolated yields. [c] Mixture of isomers with delocalized double bond.

corresponding γ-butyrolactones. We found that 2-substituted-1,2-diols containing aliphatic saturated chains such as **1a-b** provided the desired products regioselectively in moderate isolated yields (**3a-b**, 61-52%, Table 2, entries 1 and 2), while the unsaturated substrate oct-7-ene-1,2-diol (**1c**) led to the 5-substituted lactone **3c** as a mixture of isomers with the double bond delocalized along the side chain (56%, Table 2, entry 3). This result is in agreement with the well-known ability of ruthenium complexes to promote the isomerization of terminal alkenes to internal ones.[12] Additionally, the reaction also proceeds with the sterically hindered *tert*-butyl derivative **1d**, resulting **3d** in 54% yield (Table 2, entry 4). Aryl substrates such as 1-phenylethane-1,2-diol (**1e**) afforded the corresponding γ-butyrolactone **3e** too, but in lower yield (Table 2, entry 5). However, conversion of the benzylic substrate **1f** took place cleanly affording **3f** in 57% yield (Table 2, entry 6). Apart from terminal 1,2-diols, we analyzed the reactivity of internal disubstituted diols for which we chose simple cyclic compounds as model substrates (Table 2, entries 7-9). As an example, the reaction of diethyl malonate with cyclohexanediol (**1h**) led to the bicycle **3h** in a good 63% isolated yield, whereas the 5- and 8-membered ring substrates provided the desired lactones in slightly lower yields (**3g** and **3i,** 52 and 54% respectively).

After this first study and, in order to demonstrate the general applicability of this methodology, our protocol was tested by applying different malonates as coupling partner (Scheme 2). For this purpose, we selected the cyclohexanediol (**1h**) as model substrate because it was shown the most effective diol under the established conditions. First, we were intrigued about the reactivity of malonates with different alkoxy groups (**4a-e**), a relevant aspect since this methodology implies a final lactonization step so the leaving group could play an important role.[13] In this way, we observed that the reaction of **1h** (1 mmol) with dimethyl malonate (**4a**, 2 mmol) in presence of Ru-MACHO-BH (0.02 mmol) and K_2CO_3 (0.1 mmol), led to hexahydrobenzofuran-2(*3H*)-one (**3h**) in 53% yield, only slightly lower with respect to the diethyl analogue (63%, Scheme 2). Surprisingly, this transformation also proceeds effectively with bulky substrates such as di-*tert*-butyl malonate (**4b**) obtaining the same γ-butyrolactone in a good 58% yield, which demonstrates that lactonization is not a crucial step in this reaction sequence. Likewise, dibenzyl malonate (**4c**) afforded the desired product in 51% yield, however reaction with the monoester (ethyl hydrogen malonate **4d**) did not take place, which highlights the importance of basic medium for both carbon-carbon bond formation and lactonization steps.

Following this analysis, we turned our attention to the use of 2-substituted malonates **5** in this domino-process, which would allow to access trisubstituted lactones (Scheme 2).[14] With this aim, we assayed the reaction between the cyclic diol **1h** and diethyl methylmalonate (**5a**). Indeed, after 18 h at 150 °C we observed the formation of the α,β-unsaturated lactone **6a** in 55% yield. This result shows that this reaction does not undergo the classical mechanism for the Knoevenagel-type condensations. Here, due to the substitution of the malonate, the elimination of H_2O only can take place after the decarboxylation, so the double bond should be formed in the last steps of the transformation. Additionaly, the hydrogenation of the tetrasubstituted olefine under our reaction conditions does not proceed, whereby the hydrogen firstly removed from the diol would be released as H_2 in order to regenerate the catalytic species. To confirm this result, the reaction with 2-butyl malonate (**5b**) was also tested, obtaining the corresponding trisubstituted α,β-unsaturated lactone **6b** in 50% yield as a mixture of isomers. When we carried out the same experiment with diethyl phenyl malonate (**5c**) curiously we obtained both the α,β-unsaturated and saturated products in 30 and 56% yield, respectively. This result



R^4	Me	Et	*t*Bu	Bn	H, Et
Yield (%)	53	63	58	51	4

Scheme 2. Ruthenium-catalyzed synthesis of hexahydrobenzofuran-2(*3H*)-ones (**3-6**) from 1,2-cyclohexanediol (**1h**) and different malonates (**4-5**). [a] In parenthesis, yield of the saturated lactone.

suggests that the reduction of the conjugated benzylic olefine is easier than in the case of the previous aliphatic substituted malonates.

In conclusion, we have described for the first time the ruthenium pincer-catalyzed synthesis of γ-butyrolactones from easily available reagents such as 1,2-diols and malonates using borrowing-hydrogen methodology. This regioselective domino-transformation takes place through carbon-carbon bond formation by using a dehydrogenation-hydrogenation sequence, followed by intramolecular transesterification. The application of Ru-MACHO-BH as catalyst allowed the synthesis of a variety of lactones in moderate yields with the high atom economy typical of this hydrogen autotransfer process.

Notes and references

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† Electronic Supplementary Information (ESI) available: See DOI: 10.1039/c000000x/

†† Acknowledgements: We thank the state of Mecklenburg-Vorpommern and the Bundesministerium für Bildung und Forschung (BMBF) for financial support. M.P.L. thanks European Commission for a Marie Curie Intra-European Fellowship within the 7th Framework Programme (PIEF-GA-2012-328500).

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